Eesti Maaülikool
Estonian University of Life Sciences

DETERMINATION OF EMISSION FACTORS FROM ANTHROPOGENIC PARTICLE SOURCES FOR AIR EMISSION AND HEALTH IMPACT ASSESSMENT

INIMTEKKELISTE PEENOSAKESTE ERIHEIDETE MÄÄRAMINE ÕHUEMISSIOONIDE JA TERVISEMÕJUDE HINDAMISEKS

MAREK MAASIKMETS

A Thesis
for applying for the degree of Doctor of Philosophy
in Environmental Protection

Väitekiri
filosoofiadoktori kraadi taotlemiseks keskkonnakaitse erialal

Tartu 2019

Eesti Maaülikooli doktoritööd

Doctoral Theses of the Estonian University of Life Sciences

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According to verdict No 6-14/1-4 of January 23, 2019, the Doctoral Committee the Environmental Sciences and Applied Biology of the Estonian University of Life Sciences has accepted the thesis for the defence of the degree of Doctor of Philosophy in Environmental Protection.

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Defence of the thesis:
Estonian University of Life Sciences, room 2A1, Kreutzwaldi 5, Tartu on March 11th, 2019, at 10:15.

The English in the current thesis was revised by Kristoffer Hellen from Keelekord OÜ and the Estonian by Mrs. Urve Ansip.

ISSN 2382-7076
ISBN 978-9949-629-64-0 (trükis)
ISBN 978-9949-629-65-7 (pdf)

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following articles, which are referred to in the text by their Roman numerals:

I. Orru, H.; Maasikmets, M.; Lai, T.; Tamm, T.; Kaasik, M.; Kimmel, V.; Orru, K.; Merisalu, E.; Forsberg, B. (2011). Health impacts of particulate matter in five major Estonian towns: main sources of exposure and local differences. Air Quality, Atmosphere & Health, 4(3-4), 247–258.

II. Maasikmets, M.; Kupri, H-L.; Teinemaa, E.; Vainumäe, K.; Arumäe, T.; Roots, O.; Kimmel, V. (2016). Emissions from burning municipal solid waste and wood in domestic heaters. Atmospheric Pollution Research, Volume 7, Issue 3, 438–446.

III. Maasikmets, M.; Arumäe, T.; Teinemaa, E.; Kimmel, V. (Submitted). Development and preliminary assessment of a mobile non-exhaust emission measurement laboratory REAL. Submitted.

IV. Kaasik, A.; Maasikmets, M. (2013). Concentrations of airborne particulate matter, ammonia and carbon dioxide in large scale uninsulated loose housing cowsheds in Estonia. Biosystems Engineering, 114(3), 223–231.

V. Maasikmets, M.; Teinemaa, E.; Kaasik, A.; Kimmel, V. (2018). Seasonal variability of the PM and ammonia concentration in uninsulated loose-housing cowshed. Air Quality and Livestock Farming. CRC Press. Chapter 6.

The contributions from the authors to the papers are as follows:

	I	II	III	IV	V
Original idea and structure	HO, BF	ET, **MM**	ET, **MM**	AK	**MM**
Data collection	HO, MK, **MM**	**MM**, HLK, KT	**MM**, TA	AK, **MM**	**MM**, AK
Data analysis	HO, **MM**	**MM**, HLK	**MM**	AK, **MM**	**MM**
Manuscript preparation	HO, **MM**, TL, TT, MK, KO, EM, BF	**MM**, ET, HLK, VK, OR, KV, TA	**MM**, TA, ET, VK	AK, **MM**	**MM**, AK, ET, VK

HO – Hans Orru; MM – Marek Maasikmets; AK – Allan Kaasik; ET – Erik Teinemaa; VK – Veljo Kimmel; TL – Taavi Lai; TT – Tanel Tamm; MK – Marko Kaasik; KO – Kati Orru; EM – Eda Merisalu; BF – Bertil Forsberg; HLK – Hanna-Lii Kupri; KV – Keio Vainumäe; TA – Tarvo Arumäe.; OR – Ott Roots.

ABBREVATIONS

AMS - Aerosol Mass Spectrometer
BBOA - biomass burning related organic aerosol
BC – black carbon
CDCE – composition dependant collection efficiency
CH_4 – methane
Chl – chloride
CI – confidence interval
CO – carbon monoxide
CO_2 – carbon dioxide
COA – cooking related organic aerosol
DR – dilution ratio
DT – dilution tunnel
EAIA - Estonian Agricultural and Information Agency
eBC - equivalent black carbon
eBC_{bb} – equivalent black carbon from biomass burning
eBC_{ff} - equivalent black carbon from fossil fuel burning
EDB – emission database
EEA – European Environmental Agency
EF – emission factor
EI – emission inventories
EMEP - European Monitoring and Evaluation Programme
E-R function – estimated risk function
EU – European Union
FTIR - Fourier Transform Infrared spectroscopy
GHG - greenhouse gases
HCB – hexachlorobenzene
HCl – hydrogen chloride
HDV - heavy-duty vehicles
HF – hydrogen fluoride
HIA – health impact assessment
HOA - hydrocarbon-like organic aerosol

I- TEQ – International Toxic equivalency factor
IARC - International Agency for Research on Cancer
ICD-10 - International Classification of Diseases, Tenth Revision
IR – infrared
IVOC – intermediate volatile organic compounds
K^+ - potassium
kt – kilotons
LDV - light-duty vehicles
LRTAP - 1979 Convention on Long-range Transboundary Air Pollution
LU – livestock unit
LV-OOA - low-volatility oxygenated organic aerosol
ME-2 - multilinear engine algorithm
MSW - municipal solid waste
NH_3 – ammonia
NH_4^+ – ammonium
nm – nanometer
NO_3^- – nitrate
NO_x – nitrogen oxides
NR-$PM_{1.0}$ - non-refractory submicron particles
O_2 – oxygen
OA - organic aerosol
PAH - polycyclic aromatic hydrocarbons
PCB - polychlorinated biphenyls
PCDD/F - dibenzo-p-dioxins and furans
PM – particle mass concentration
PM_{10} – particles10 micrometers or less in aerodynamic diameter
$PM_{2.5}$ – fine particles 2.5 micrometers or less in aerodynamic diameter
PN – particle number concentration
POA - primary organic aerosol
Q-ACSM – Quadrupole Aerosol Chemical Speciation Monitor
REAL - Road Emission Aerosol Laboratory
RF - response factor
RIE - relative ionization efficiency
RWC - residential wood combustion

SA – source apportionment
SIA - secondary inorganic aerosol
SO_2 – sulphur dioxide
SO_4^{2-} – sulphate
SOA - secondary organic aerosol
SP – solid particles
SVOC – semi-volatile organic compounds
SV-OOA - semi-volatile oxygenated organic aerosol
TMR feeding - total mixed ration feeding
WHO – World Health Organization
VOC – volatile organic compounds
WS-CRDS - Wavelength-Scanned Cavity Ringdown Spectroscopy
YLL - years of life lost
μm – micrometer

1. INTRODUCTION

Air pollution has become the world's top environmental cause of premature mortality, overtaking dirty water and poor sanitation (OECD, 2012). It has been estimated that air pollution (ambient and indoor air) causes around 6 million premature deaths annually (Landrigan et al., 2018). WHO's International Agency for Research on Cancer (IARC) concluded in 2013 that outdoor air pollution is carcinogenic to humans, with the particulate matter (PM) component of air pollution most closely associated with increased cancer incidence (Loomis et al., 2013).

Anthropogenic emissions leading to atmospheric aerosols have increased dramatically over the past century (Seinfeld, 2015). Klimont et al. (2017) estimate that global emission rates of PM have not changed significantly between 1990 and 2010, showing a strong decoupling from the global increase in energy consumption.

In general, the major sources of air pollution in European urban areas are still biomass burning, road transport, industry and agricultural emission sources. Some anthropogenic air pollutants are released into atmosphere intentionally while other are released as unavoidable by-products or waste products (Chandrappa and Chandra Kulshrestha, 2016). Household fuel usage is the most significant source of emissions of primary particulate matter (PM_{10}) and fine particles ($PM_{2.5}$), and has increased their emission by 13% and 11%, respectively, since 2003 (EEA, 2014). Biomass burning (primarily of wood) for residential space heating as well as for energy production is now a growing source of fine PM emissions in the European Union (EU) (Sigsgaard et al., 2015). As biomass has been promoted as a renewable fuel in the context of climate change mitigation policies, it has led to increased biomass usage in the household sector, but without adequate emission controls (EEA, 2018a). Emissions from smaller installations are significant due to their large quantity, varied types of combustion techniques and range of combustion efficiency. Many of them have no abatement measures or are relatively inefficient (EEA, 2013). Even further, there is a remarkable share of the population, even in developed countries, that burns domestic waste in open fires and in household heating stoves (Solorzano-Ochoa et al., 2012). This should be taken into account when emission inventories are compiled and air quality assessments are performed.

Emissions from road transport contributes to approximately 11% of the total $PM_{2.5}$ emissions in Europe, but accounts for one quarter of the reduction in total European emissions since 1990 (EEA, 2018a). Exhaust emissions from traffic have been estimated to decrease further due to policy measures applied in that sector (Font and Fuller, 2016; Harrison and Beddows, 2017; Kousoulidou et al., 2008; Rexeis and Hausberger, 2009). Non-exhaust traffic emissions are estimated to comprise about 50% of the exhaust emissions of primary PM_{10}, and about 22% of the exhaust emissions of primary $PM_{2.5}$ (Hak et al., 2009). Even with zero tail-pipe emissions, traffic would continue to contribute to PM emissions through non-exhaust emissions (Dahl et al., 2006). Rexeis and Hausberger (2009) have found that the percentage of non-exhaust PM of the total PM emissions will increase from about 50% at the beginning of this decade up to 80–90% by the end of the next decade. In Nordic countries studded tyres, which are used to increase traction and road safety during icy and snowy conditions, increase non-exhaust emissions even further and should be taken into account when air quality and emission studies in those areas are compiled (Gustafsson et al., 2018).

Agricultural production, processing, and distribution generate substantial air pollutants, mainly greenhouse gases (GHG), ammonia (NH_3) and PM (Sun et al., 2017). Emissions from agriculture either decreased very little and not at all in the decade of 2003–2013 in Europe (EEA, 2013). In the period of 2013–2016, NH_3 emissions increased in the agriculture sector by about 3% (EEA, 2018b) and remarkable amounts of air pollution continue to be emitted (Chandrappa and Chandra Kulshrestha, 2016). Agriculture, is responsible for most (92%) of the NH_3 emissions, 15% of PM_{10} and 4% of $PM_{2.5}$ emissions in the EU (EEA, 2018b). It is a significant pollution source in intensive agricultural areas. NH_3, which is the main air pollutant emitted from livestock farming, also plays a role in atmospheric reactions (e.g., gas-to-particle conversion). Once airborne, it forms ammonium aerosols such as ammonium sulfate, ammonium nitrate and ammonium chloride. Particles formed with NH_3 may contribute to a high share of the total mass of fine particles (Hristov, 2011), which makes NH_3 an important component in particle formation processes (Xu and Penner, 2012). It has been estimated that through secondary inorganic aerosol (SIA) formation, the agricultural sector contributes through NH_3 emissions 10–20% of the fine particle mass in densely populated areas in Europe (Brunekreef et al., 2015). Still

to this day, the specific impacts of livestock PM on human and animal health has been poorly studied.

At the EU level, many regulations regarding air pollution reduction have been established and remarkable emission reduction during the past years from the industry sector has been achieved (EEA, 2018b). Nevertheless, more than 80% of the population in the WHO European Region (including the EU) lives in cities with levels of PM exceeding WHO Air Quality Guidelines (WHO, 2013). There are still a multitude of emissions which are emitted diffusely and are not regulated at the EU level. Those emissions are important and the impact of reducing them would be remarkable.

Therefore, the main focus of the thesis is to assess PM emissions from major anthropogenic sources and identify emission sources of PM precursors as PM is remarkably reducing the overall air quality in Europe and in Estonia. The PM precursors may contribute significantly to PM emissions at the national level but have been poorly studied so far.

2. REVIEW OF THE LITERATURE

2.1. Air pollution

Air pollution is a mixture of particles of any chemical, physical or biological agents and gases in the air that modifies the natural characteristics of the atmosphere. Air pollution in such a form refers to the contamination of the air either outdoors or indoors, detrimental to the environment and human health. One of the major health concerns is premature mortality which is connected to a wide range of pollutants, including particulate matter and fine particles (Burnett et al., 2014). Fine particles are thought to pose a particularly great risk to health because they are more likely to be toxic than larger particles and can be breathed more deeply into the lungs (Xing et al., 2016). In addition to the direct health effects, Orru et al. (2015) found that PM exposure also negatively affects subjective assessments of well-being. In order to take action to reduce exposure to air pollution, and its associated health impacts, it is essential to know the sources and activities contributing to local air pollution exposure (Karagulian et al., 2015).

2.2. Particles

Particles may be emitted directly as primary aerosols[1] or formed in the atmosphere by gas-to-particle conversion processes (secondary aerosols). Atmospheric aerosols are generally considered to be particles that range in size from a few nanometers (nm) to tens of micrometers (μm) in diameter (Seinfeld and Pandis, 2006). As seen in Figure 1, particles can change their size and composition through condensation of vapour, evaporation, coagulating with other particles, chemical reaction, or activation in the presence of water supersaturation to become fog and cloud droplets (Seinfeld and Pandis, 2006).

1 An aerosol is technically defined as a suspension of fine solid or liquid particles in a gas, but common usage refers to the aerosol as the particulate component only (Seinfeld & Pandis, 2006)

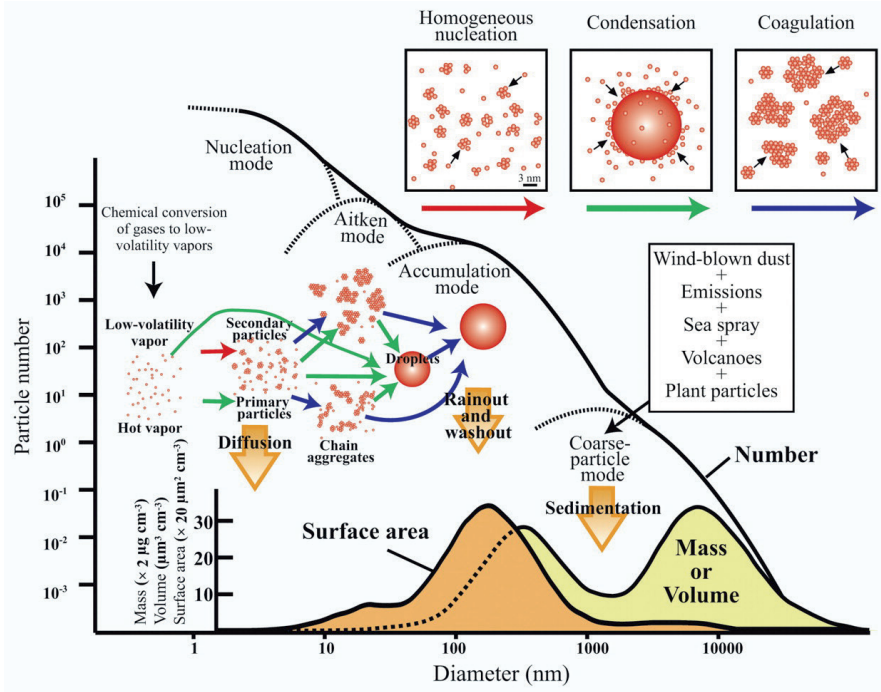

Figure 1. Schematic of the size distribution of aerosol particles for various parameters (Buseck and Adachi, 2008)

Whereas larger particles are derived chiefly from soil and other crustal materials, fine particles are derived primarily from the combustion of fuels in transportation, manufacturing, and power generation. Fine particles typically contain a mixture of particles including soot, acid condensates, sulfate and nitrate (Dockery et al., 1993). According to the formation process, primary and secondary aerosols can be distinguished. In addition, inorganic and organic aerosols can be distinguished. The relative contribution of primary organic aerosol (POA) and secondary organic aerosol (SOA) to the overall organic aerosol (OA) mass remains controversial (Robinson et al., 2007). Primary aerosols are emitted directly as particles, whereas secondary aerosols are formed in the atmosphere through chemical reactions that convert more volatile substances into lower volatility products, which then enter into the particulate phase (Aiken et al., 2008). The most prominent secondary aerosol precursor gases are NH_3, NOx, SO_2, and volatile organic compounds (VOCs) (Vandyck et al., 2018). A large fraction of fine particles is organic material, typically 20–90% (Jimenez et al., 2009). The current understanding of OA emissions suggests that more than half of the organic matter emitted from transportation sources and wood combustion actually

evaporates as it is diluted in the atmosphere (Robinson et al., 2007). The resulting organic vapours can be oxidized in the gas phase and by re-condensation, forming oxygenated organic aerosols. Further oxidation ('chemical aging') of semi and intermediate volatility organic compounds (SVOCs and IVOCs) can be important in the formation of secondary aerosols (Robinson et al., 2007). Carbonaceous aerosols, by-products of incomplete combustion, absorb sunlight and can therefore heat the atmosphere. In addition aerosol direct radiative forcing may weaken the boundary-layer mixing, thus have influence on the aerosol distribution near the surface (Toll et al., 2015). However, our understanding of the complex interactions between cooling and heating aerosols remains limited (Samset, 2018). The most commonly measured aerosol property is the mass or number concentration of particulate matter (PM) in a unit volume of gas, mostly expressed as $\mu g/m^3$ or number/cm^3.

2.3. Health effects of particles

One of the most important triggers of air pollution-related health effects are PM_{10} and $PM_{2.5}$, which are currently considered to be the best indicators for the health effects of ambient air pollution (Burnett et al., 2014). Currently the permitted values of PM_{10}, and $PM_{2.5}$ are frequently exceeded in Europe (EEA, 2018a), posing a significant risk to public health (EEA, 2009). Moreover, epidemiological studies show that health effects might appear even at lower levels than the current limit values (ERS et al., 2006) and available data has not established any firm threshold value (Anderson, 2009; Barnett, 2014; Chen and Kan, 2008).

PM has been widely studied and associated with numerous health outcomes either from short-term or long-term exposure. Many short-term exposure studies have focussed on the relationships between PM and mortality and morbidity. There have also been several meta-analyses of these studies (Atkinson et al., 2014), some of which provide pooled effect estimates (Anderson et al., 2005; COMEAP, 2015; WHO, 2013).

Moreover, long-term exposure to PM over years or decades leads to chronic health problems such as cardiovascular disease, cardiopulmonary disease, and lung cancer. The associations between particles and increased mortality have been shown in cohort studies conducted in the United States (Abbey et al., 1999; Bentayeb et al., 2015; Di et al., 2017; Dockery et al., 1993; Jerrett et al., 2005; McDonnell et al., 2000; Pope et al., 2018;

Pope et al., 2002; Pope et al., 1995; Thurston et al., 2016; Turner et al., 2016; Turner et al., 2017) and Europe (Beelen et al., 2015; Bentayeb et al., 2015; Filleul et al., 2005; Gehring et al., 2006; Hoek et al., 2002; Naess et al., 2007; Raaschou-Nielsen et al., 2013). However, the results of the studies are inconsistent. The contradictions are likely due to different exposure metrics, as well as slightly varied outcome endpoints.

It is believed that the negative effects of particles are mostly related to chronic cardiopulmonary diseases (Pope and Dockery, 2006; Schwarze et al., 2006; WHO, 2013). Other health effects of particles include diabetes (Thiering and Heinrich, 2015), rheumatic diseases (Sun et al., 2016), cognitive functioning (Clifford et al., 2016), neurodegenerative diseases (Oudin et al., 2016; Xu et al., 2016) and birth effects, such as preterm birth and low birth weight (Li et al., 2017).

PM with its components (e.g. polycyclic aromatic hydrocarbons, PAH; volatile organic compounds, VOC) are able to induce inflammatory processes and cause activation of redox mechanisms and oxidative stress (Adams et al., 2015; Brook, 2008; Nel, 2005; Pope and Dockery, 2006; Thurston et al., 2013). However, the components and fractions of particulate pollutants related to adverse health effects are still not fully understood. Therefore, particles are largely used as an indicator of toxic air pollutants in epidemiological studies (WHO, 2016). A $PM_{2.5}$ increment of 10 $\mu g/m^3$ has been associated with an increase in the risk of mortality, but the mass concentration alone might not be sufficient to evaluate the health effects of particles, as certain chemical components and sources are more harmful than others (Zanobetti et al., 2014). Many studies show that the smaller the PM size, the higher the toxicity through mechanisms of oxidative stress and inflammation (Chen et al., 2016; HEI, 2013; Valavanidis et al., 2008). Nevertheless, reviews of epidemiological studies have shown that there seem to be ambiguous health effects resulting from coarse particles ($PM_{2.5–10}$) as well (Adar et al., 2014; Brunekreef and Forsberg, 2005). According to Brunekreef and Forsberg (2005), acute exposure to coarse PM may be significantly associated with mortality and morbidity (especially respiratory-related hospital admissions).

The benefits of improved air quality include a reduction in premature mortality due to related cardiovascular and respiratory diseases and lung cancer (Cohen et al., 2017).

2.4. Main anthropogenic sources of particles in the urban environment

The main source of urban air pollution is mostly anthropogenic processes. Karagulian et al. (2015) has estimated that globally 25% of urban ambient air pollution from $PM_{2.5}$ is contributed by traffic, 15% by industrial activities, 20% by domestic fuel burning, 22% from unspecified sources of human origin, and 18% from natural dust and salt. It has been found that the main contributors to fine PM are organic materials followed by sulphate, nitrate, ammonium and black carbon (BC) (Putaud et al., 2004; Putaud et al., 2010). But the emission sources may differ depending on the location and meteorological conditions (Aurela et al., 2015). During the last decade much scientific attention has been paid to source apportionment (SA) studies and much of it has focused on urban and rural air quality. Six categories of main sources of ambient PM are commonly identified in SA studies: traffic, industry, domestic fuel burning, natural sources (including soil dust [re-suspended] and sea salt), and unspecified sources of pollution of human origin (Karagulian et al., 2015; Mohr et al., 2012).

Apart from the physical and chemical state of pollutants, it is also important to consider the geographical location and distribution of sources (WHO, 2005a). For the pollutant emission estimation, emission inventories at the global or local level are often used. An emission inventory is the foundation for air quality management, as from the inventory it is possible to understand the relations between (human) activities, technologies, and the release of pollutants (Denier van der Gon et al., 2018). Within emission inventories, estimates of emissions from a pollution source are based on a technique that uses emission factors (EF). Those are based on source-specific emission measurements as a function of activity level (e.g., amount of annual production at an industrial facility) with regard to each source (Seinfeld and Pandis, 2006). At the present time, no emission inventory covers all species, sectors and years of interest for environmental impact studies. Therefore, a collection of inventories of different origins and quality are used in atmospheric models (Monks et al., 2009). Emission inventories, in combination with dispersion models, are a powerful tool for estimation or prediction of ambient air concentrations, but the quality of the outcome depends largely on the input data used like EF and activity data.

For the health impact assessments, adequate EF and emission databases (EDB) are needed. For the validation of EF and EDB, dispersion models in conjunction with ambient air monitoring results, are encouraged to be used (Fairmode, 2010). Therefore, the quality of country-specific emission inventories largely depends on reliable activity and emission data. Verified EF are needed for the annual air pollutants emission reporting at the national and international (e.g. the 1979 Convention on Long-range Transboundary Air Pollution [LRTAP]) levels. Most of the European countries use the EMEP/EEA air pollutant emission inventory guidebook (EEA, 2013) for the emission inventories where the given EF are sometimes highly uncertain and may not take into account country-specific circumstances. Therefore, further efforts are required to improve data availability and evaluation (Karagulian et al., 2015). Using country-specific EF is encouraged to get more reliable emission inventories. In-field measurements make a better database for inventory EF, as they take into account several important factors for the level of the pollutant emissions, which for example in fuel combustion sector may include the co-incineration of wastes, the complete system consisting of combustion unit, flue pipe and chimney, memory effects in the chimney and the habitual practices of the operators (Hübner et al., 2005). These factors should be considered when compiling the national emission inventories and therefore, it is crucial to have EF measurements that represent, in a more accurate way, the real situation in a country.

2.4.1. Wood burning emissions from the residential sector

Biomass is an important source of renewable energy and has been favoured due the climate policy to reduce the anthropogenic CO_2 emissions, but on the other hand this has led to higher PM, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins and furans (PCDD/F), and hexachlorobenzene (HCB) emissions from the small scale wood combustion sector (EEA, 2014). Increased biomass production may indirectly affect land use and emissions of biogenic VOC (Maas and Grennfelt, 2016). Sigsgaard et al. (2015) concluded that emissions from current biomass combustion products negatively affect respiratory and, possibly, cardiovascular health in Europe and it is estimated that ambient PM from residential heating with wood and coal is responsible for 61,000 premature deaths per year in the EU28 (Chafe et al., 2015). It has been found that biomass combustion is a major global source of PM in the atmosphere with significant impacts on regional

air quality, visibility, ecosystems, human health, and global climate (Hobbs et al., 1997). In Central and Eastern Europe biomass burning-related PM contribute to about 32% of the total $PM_{2.5}$ concentration on average (Karagulian et al., 2015). Carbonaceous aerosols, which are often by-products of incomplete combustion, absorb sunlight and can thereby heat the atmosphere (Samset, 2018) and in addition it may lead to weakening of boundary layer mixing, thus have impact on aerosol distribution near surface (Toll et al., 2015). Once released into the atmosphere, biomass smoke is mixed with the particles emitted from many other natural and anthropogenic pollution sources and are in many cases difficult to recognize and quantify (Simoneit et al., 1999).

Besides combustion in large heat and power plants, residential biofuel burning is employed for heating and cooking. In cold areas, biomass (mainly wood) is burned for heating (Johansson et al., 2004). In Nordic countries, wood is typically used as an primary or auxiliary heat source in one-family houses, mainly in masonry heaters and different types of stoves (Tissari et al., 2009). Due to incomplete combustion, which often occurs in domestic heating, organic material in the presence of chlorine causes the formation of chlorinated organic by-products, such as PCDDs, polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and HCB (Hedman et al., 2006). Additionally, PAHs and BC are emitted during the incomplete burning of biomass, which may have high toxicity (Fernandez et al., 2001).

Burning of waste, whether at individual residences, businesses, or dump sites, is a significant source of airborne pollutants. However, waste burning is not included in many emission inventories currently used for chemistry and climate modelling applications (Wiedinmyer et al., 2014). Waste burning can be an important organic aerosol source but there are only a few studies on it available (Mohr et al., 2009). Burning of plastics releases high concentrations of extractable organic compounds that cause various problems in developing and developed countries (Barabad et al., 2018). There is an estimation that emissions of PM_{10} from the open burning of domestic waste in China is equivalent to 22% of China's total reported anthropogenic PM_{10} emissions (Wiedinmyer et al., 2014). Waste burning may be one important source of aerosols, which has been largely overlooked. It is estimated that around 40 percent of the world's waste is disposed of in this reckless and toxic manner (Wiedinmyer et al., 2014). Under difficult economic conditions

people tend to burn more household waste, the emissions of which are of special concern regarding human health, as elevated levels of fine particles and dioxins may occur (WHO, 2015). Modelling studies have suggested that the use of municipal solid waste (MSW) in burning processes may reduce the combustion efficiency (Moran et al., 2009) and lead to an increase in toxic air pollutants (Edo et al., 2018; Hedman et al., 2006). It has been reported that the release of PM through waste burning can cause deterioration in individuals with pre-existing conditions such as bronchitis, asthma, and emphysema (USEPA, 2016). Due to the low height of residential emission sources, pollution accumulates mostly near the source, as dilution by dispersion is minimal. Thus the burning of waste in household stoves or in backyards may lead to very high concentrations near and inside the households and may affect the health of persons living there.

Altogether biomass burning in heaters and fireplaces in households is estimated to account for around 37% of $PM_{2.5}$, 44% of BC, 46% of PAH, 22.5 % of PCDD/F and 60% of HCB emissions in Estonia in 2016 (EEEA, 2018a). There is, however, a lack of information concerning the characterisation of particulate emissions from small-scale biomass burning systems in which some municipal solid waste (MSW) is burned along with the wood logs as this habit is still common in many countries worldwide (Kupri et al., 2018; Mohr et al., 2009; Wiedinmyer et al., 2014).

2.4.2. Non-exhaust emissions

Over the last two decades most of the attention regarding emission reduction has been focused on vehicle exhaust emissions and their successful remediation and regulation, but nowadays about half of traffic emissions derive from non-exhaust-related processes (Amato, 2018). According to Padoan and Amato (2018) vehicles' non-exhaust emissions include the following emission sub-sources:

1. Direct brake wear;
2. Direct tyre wear;
3. Direct road wear;
4. Road dust suspension.

Estimation of non-exhaust traffic emissions is noteworthy, as earlier studies have shown that particulate emissions from this sector have a

significant effect on urban air quality (Amato et al., 2014; Bukowiecki et al., 2010). Studies in several European cities have shown that about half of total fine particulate emissions are made up of particulates originating from surface wear. In European countries that use traction sand, salting and studded tyres against skidding in winter, the PM_{10} fraction originating from surface wear, can reach 90% (Forsberg et al., 2005b; Omstedt et al., 2005). Non-exhaust emissions have been predicted to increase in relative importance to urban PM mass during the last two decades due to the reduction of exhaust emissions (Kousoulidou et al., 2008; Rexeis and Hausberger, 2009). Therefore suspended road dust will remain a problem because of the increasing number of vehicles in urban and rural areas. Literature data about the real-world measurements of road dust resuspension is scarce to date. For the non-exhaust emission estimation the following approaches are mainly used:

1. Mobile platform measurements (Etyemezian et al., 2003; Hussein et al., 2008; Mathissen et al., 2012; Pirjola et al., 2009);
2. Ambient air upwind-downwind measurements in combination with receptor models (Bukowiecki et al., 2010; Denby et al., 2013a; Denby et al., 2013b; Ferm and Sjöberg, 2015; Pirjola et al., 2012).

There is still a knowledge gap regarding the dominant mechanisms leading to road dust emissions, although resuspension of surface particle loading obviously plays an important role (Pirjola et al., 2010). Furthermore, until now many EU countries have not reported their non-exhaust emissions in annual emission inventories (EI) and this has been seen as one of the reasons why dispersion models underestimate PM_{10} concentrations (Amato et al., 2014), which makes this area lucrative for further research.

2.4.3. Livestock farming emissions

Livestock production is a major contributor to NH_3 emissions (Groot Koerkamp et al., 1998; Steinfeld et al., 2006). In the last 100 years, global NH_3 emissions have increased from 10 Tg/yr to 37 Tg/yr (Lamarque et al., 2010) and this increase is entirely attributable to NH_3 emissions from agriculture (Beusen et al., 2008). NH_3 is an important atmospheric pollutant with a wide variety of impacts (Beusen et al., 2008). Gaseous NH_3 emissions from livestock production inter alia are deemed responsible for the acidification of several ecosystems and also for the

formation of secondary particles (Bluteau et al., 2009; Cambra-López et al., 2010). NH_3 released from near-surface sources into the atmosphere generally has a relatively short lifetime of 1–5 days and may deposit near the source through dry or wet deposition processes. NH_3 can also participate in atmospheric reactions (e.g., gas-to-particle conversion) once airborne, forming ammonium aerosols such as ammonium sulphate, ammonium nitrate, and ammonium chloride. It tends to have a long atmospheric residence lifetime (1–15 days) due to a decrease in dry deposition velocity (Aneja et al., 1998) and therefore may be transported and deposited further downwind from the source (Blunden et al., 2008). It has been shown that 50% of the available NH_3 was converted to NH_4^+ in about 35 minutes at concentration levels of 2.7 $\mu g/m^3$ (McKay, 1971). A large portion of atmospheric aerosols, acting as cloud condensation nuclei, consists of sulfate neutralized to various extents by NH_3 (Graedel et al., 1993).

Recent studies have shown that livestock farming contributes to anthropogenic $PM_{2.5}$ levels, which leads mainly to elevated levels of secondary inorganic aerosols, including ammonium sulfate and ammonium nitrate (Bauer et al., 2016; Brunekreef et al., 2015; Lelieveld et al., 2015).

3. AIM OF THE THESIS

The aim of this thesis is to measure and evaluate emission factors for important anthropogenic particle sources.

Hypothesis:

1. Uncertainty in results of air quality modelling and health impact assessment depends on the quality of air pollution emission data.

2. Residential wood combustion, non-exhaust emissions from the road transport and livestock farming emissions have a significant impact on air quality in cities.

The specific objectives of the thesis are the following:

1. To determine the health impacts of particulate air pollution in major cities in Estonia based on default (non-country-specific) emission factors.

2. To specify country-specific EF for residential heating appliances, for the non-exhaust and for the livestock farming sources.

3. To validate the measured EF using dispersion modelling techniques and discuss data quality in the context of air pollutants' emission inventory and impact assessments.

4. MATERIALS AND METHODS

4.1. Assessments of health impacts (Paper I)

The health impacts of particle concentrations were planned to be estimated in Tallinn, Tartu, Kohtla-Järve, Narva and Pärnu.

First, the annual levels of $PM_{2.5}$ were modelled using the Airviro Eulerian Advection-Diffusion grid dispersion model with grid resolution of 200 × 200 meters. Airviro uses data on emissions, measured levels from air pollution monitoring stations, and meteorological variables from meteorological stations. This data is used to conduct the air pollution dispersion modelling and mapping. The average concentration of grid cells in a neighbourhood was assigned as the typical long-term exposure to all residents of that neighbourhood.

Second, we used daily average concentrations of PM_{10} in the monitoring stations in 2006 in Tallinn and in 2008 in Kohtla-Järve. In Tartu, Narva and Pärnu the daily PM_{10} concentrations were modelled for 2008. The modelling results were validated with real monitoring data in Tallinn and Kohtla-Järve (stations operated during the whole study period), Tartu and Narva (stations opened summer and fall 2008). For additional model validation, measurement campaigns were conducted in Tartu, Narva, and Pärnu using FH 62-I-R β-radiation absorption equipment.

Third, the population residency data for Tallinn was obtained from the Estonian Population Register for 2006 and for other cities based on population census data from 2000 and was sorted according to address and registration into different age groups. The citizens' residences were sorted into neighbourhoods (regions with similar geographical, socio-economic, etc. patterns used in city planning and management) to identify site-specific exposure to air pollution and identify the areas of greatest risk. The baseline total mortality (ICD-10 categories A00-Y98) and hospitalization (cardiovascular [ICD-10 categories I00-I99] and respiratory causes [ICD-10 categories J00-J99]) data was retrieved from Statistics of Estonia and from the Estonian Health Insurance Fund (EHIF) for 2006 and 2007.

Fourth, from the exposure assessment for HIA calculation, the natural background was subtracted, as there are likely no effects below these levels (probable threshold value). As fine particles were not measured during that time in Estonian rural areas, the annual concentration (~5 $\mu g/m^3$) in nearby areas of Helsinki was implemented (YTV, 2008).

Fifth, the following exposure-response relationships from previous studies were used: for total mortality 6.2 percent (95% CI 1.6–11%) per 10 $\mu g/m^3$ increase of annual mean $PM_{2.5}$ concentration (Pope et al., 2002) and 1.14 percent (95% CI 0.62–1.67%), and 0.73 percent (95% CI 0.47–0.93%) per 10 $\mu g/m^3$ increase of PM_{10} daily averages for respiratory (Atkinson et al., 2004) and cardiovascular hospitalizations (COMEAP, 2006), respectively.

Based on this data, the number of years of life lost (YLL) and decrease of life expectancy were assessed using the WHO software AirQ 2.2.3 in all 142 neighbourhoods. The number of hospitalizations was determined with AirQ at different exposure intervals (10–19.9 $\mu g/m^3$; 20–29.9 $\mu g/m^3$; etc.) in Tallinn, Tartu, Kohtla-Järve, Narva, and Pärnu. To calculate short-term exposure effects, no effect was assumed below 10 $\mu g/m^3$.

The methodology for calculation of external costs is described in more detail in the study of Orru et al. (2009b).

4.2. Biomass and MSW burning emission measurements (Paper II)

Country-specific residential wood burning EF, including historical EF, with wood log and MSW co-burning were measured for the revision of the national air pollutants emission inventory and to identify its possible effects on air quality. Including historical EF was important for the revision of the national emission inventory and to evaluate possible changes in MSW burning and possible toxic pollutant emissions during previous years.

Six experiments with three tests for each reference year (1990, 1995, 2000, 2005, 2010 and 2013) were conducted using firewood mixed with common MSW in a way that different types of materials within the combustible waste material group were present. All tests were conducted at the Estonian Environmental Research Centre's stove

laboratory, where PM, PCDD/F, HCB, PAH and gaseous pollutants were measured. All samples were taken from the hot flue gas from a typical Estonian masonry heater that was chosen for conducting the experiments, as around 80% of households use masonry heaters or stoves for heating and cooking purposes (Loosaar et al., 2008). Based on interviews given by many potters and chimney sweeps, during the experiments the heater door was open around 10% of its full capacity, as this is consistent with the heating habits of most of the population. As the draught in household chimneys is strongly influenced by the ambient conditions, a flue gas blower at the top of the chimney was used. Using a flue gas blower, it was possible to establish similar draught conditions (flue gas speed in chimney around 1.5 to 2 m/s) in all 18 experiments (Paper II).

The wood moisture content ranged between 14% and 18%. The fuel net calorific value measured in all 18 experiments was 20.399 ± 0.662 MJ/kg. Analysis showed that the average chlorine content of the mixed fuel was 0.101 ± 0.034%. Fuel was ignited from the bottom, as this is the most common method used by most of the heater users in Estonia. MSW was sourced from the Estonian Environmental Research Centre's kitchen, different households and the package waste receptacle of an apartment building (Paper II).

Wood and MSW burning experiments are based on the amount of MSW generated by Estonia's average household. Estonian average households are relatively small: according to Estonia's statistics information from 2011, the average household size is 2.13 people (Statistics Estonia, 2014). To calculate the amount of MSW burned per household, a family of three as an average is taken into account in any observed year (Paper II). It can be assumed that people tend to burn flammable materials consisting of plastic, paper, cardboard, wood, textiles, and other flammable wastes. A more detailed overview of the consistency of MSW included in the experiments is described by Kupri (2015a).

PM concentrations were sampled using a Dekati® Diluter (2-stage dilution), where the sampling line was heated up to 180°C and the filtered dilution air provided by the compressor was heated in the first stage up to 180°C. For the second dilution stage, filtered dilution air at room temperature (around 20°C) was provided. For the PMx measurement ELPI (Dekati®, 13 size classes in range of 0.03–10 μm) and ELPI+

(Dekati®, 15 size classes in range of 0.006–10 μm) were used (Paper II). The ELPI impactors cover the size range of 28 nm to 10.04 μm, with D50% aerodynamic cut points of 28 nm, 54 nm, 93 nm, 156 nm, 264 nm, 386 nm, 619 nm, 957 nm, 1.61 μm, 2.41 μm, 4.03 μm, 6.65 μm and 10.04 μm, respectively, for stages 1–13. The ELPI+ impactors cover the size range of 6 nm to 9.86 μm, with D50% aerodynamic cut points of 6 nm, 15.5 nm, 30.2 nm, 53.7 nm, 93.4 nm, 153 nm, 253 nm, 378 nm, 598 nm, 940 nm, 1.62 μm, 2.45 μm, 3.63 μm, 5.33 μm and 9.81 μm, respectively, for stages 1–15.

For the PCDD/F, HCB and PAH sample collection, an EVA Dioxin Sampler 1.5 E-type (Metlab Miljö AB) was used. All samples were taken from the hot flue gas according to standard EVS-EN 1948-1 (2006) (Paper II).

Gas concentrations (SO_2, NO_x, CO, CO_2, HCl, HF, CH_4, O_2 and 11 calibrated volatile organic compounds) were analysed, temperature (°C) and water content (%) were measured during the whole burning process using a Fourier Transform Infrared (FTIR, Gasmet Technologies Ltd.) analyser (Paper II).

Measured pollutants concentrations were normalized according to methods described by Tissari (2008) and Van Loo and Koppejan (2008). EF were calculated according to Tissari (2008) and Ministerial regulation no 59 (2016).

Later, the weighted $PM_{2.5}$ EF from Paper II incorporating results from previous studies (Maasikmets et al., 2015b; Teinemaa et al., 2013) was calculated and is described in more detail in section 4.5.

4.3. Non-exhaust PM emission measurements (Paper III)

Using results from other studies (Hussein et al., 2008; Mathissen et al., 2012; Pirjola et al., 2009), a mobile measurement laboratory REAL (Road Emission Aerosol Laboratory) was built for measuring PM originating from vehicle tyres, brake pads and road pavement abrasion (Figure 2).

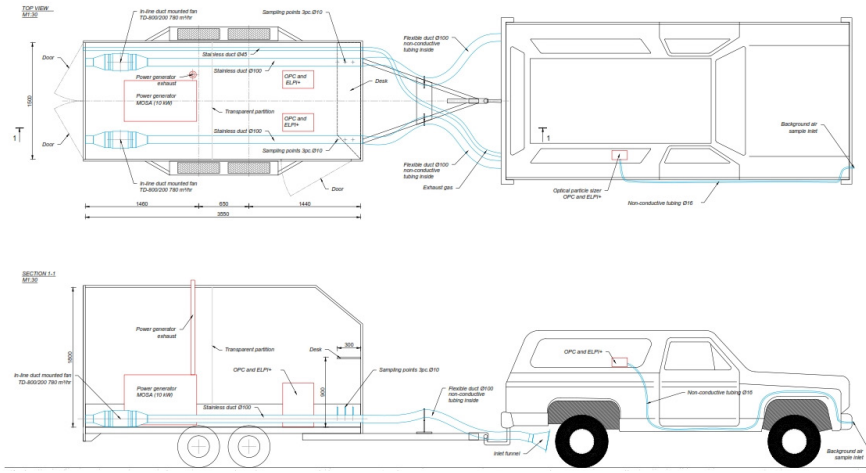

Figure 2. Schematic view of REAL (Paper III)

The sampling of PM was done directly behind both back wheels of the vehicle and the PM background concentrations were measured in front of the vehicle. The REAL measurement system can also measure vehicle exhaust gases under field conditions (Paper III).

To prevent entry of moisture and splashes into the measurement system (which would affect the accumulation of particulates) the device can only be used in dry weather and on relatively dry road conditions. Other weather conditions, like wind velocity and temperature, have little effect on the measurement, as long as sampling is done at the centre of the tyre and not further than 10 cm from the tyre surface (Etyemezian et al., 2003).

Altogether four tests with studded and non-studded tyres were done in April 2013, at a time when use of winter tyres is still allowed in Estonia. Tests with summer tyres (five altogether) were done in summer 2013 and 2015 and more details about the technical setup can be found in Paper III. During the measurement, rear-wheel drive was used. The trailer-housed particle analyser Dekati ELPI+ (size range 6 nm–10 μm, Electrical Low Pressure Impactor, Dekati Ltd), its pump, optical particle analyser OPS (size range 300 nm–10 μm, Optical Particle Sizer 3330, TSI Ltd), an air compressor for cleaning thermal sensors (GIS, SIL AIR 50/9, Silentaire Technology Ltd), and other equipment (electric generator, sampling probes with adjustable fans, controller computer, data loggers for thermal sensors, UPS and electrical switchboard) (Paper III). The ELPI+ impactors cover the size range of 6 nm to 9.86 μm,

with D50% aerodynamic cut points of 6 nm, 15.5 nm, 30.2 nm, 53.7 nm, 93.4 nm, 153 nm, 253 nm, 378 nm, 598 nm, 940 nm, 1.62 μm, 2.45 μm, 3.63 μm, 5.33 μm and 9.81 μm, respectively, for stages 1–15.

Compact infrared temperature sensors (Optris CT LT, Optris GmbH) that measured tyre and road surface temperatures were attached to the footboard of the vehicle. These sensors determine the temperature of an object's surface using an infrared sensor. A tyre temperature sensor was positioned horizontally, so that it could be pointed directly at the tyre. A pavement temperature sensor was positioned vertically, so that it could be pointed directly at the pavement. Filtered compressed air was directed to both sensors 1–2 litres/min to keep them clean and prevent errors due to surrounding dust. Electricity for the analysers and other equipment was produced by a diesel generator (GE 12000 LD/GS, MOSA, BCS Group) with a capacity of 10 kW. Diesel generator exhaust gas was directed out through the roof and thus did not affect measurement results. The vehicle was equipped with a GPS that could record vehicle coordinates (in degrees) and speed (in km/h) at 5-second intervals (Paper III).

A special sampling inlet, with a surface area of 400 cm^2 and a sieve with a pit diameter of 3 mm preventing entry of large particles, was installed in the vehicle's wheel arch. Two sampling probes with a diameter of 100 mm and length of 3,000 mm (non-conductive tubing inside a flexible probe between the vehicle and the trailer) + 3,563 mm (a probe in the trailer fixed horizontally to the floor of the trailer) were used. Excess air exited via openings in the rear doors of the trailer. Both sampling probes had three 10 mm diameter vertical sampling points that provided sample to the analysers. An ELPI+ thermal sensor was fitted in the sampling probe for measuring the temperature of the analysed air. The trailer also contained a 50 mm diameter probe for vehicle exhaust gas that was vented to the back of the trailer and routed the vehicle exhaust gas away from the sampling point. To allow isokinetic sampling, the sampling probes were fitted with adjustable suction fans at the end (TD-800/200, max suction 2 × 1100 m^3/h). The air speed inside the probes was spot-checked via pressure difference using a Testo 400 automated analyser (Testo AG, GmbH) (Paper III).

To measure the background air, a non-conductive sampling probe was fitted to the front bumper of the vehicle from where the background air was sampled by another set of OPS and ELPI+ (Paper III).

Using measured concentrations, PM_{10} EF (milligrams per kilometre of travel, mg/vkm) were calculated using the equations described by Mathissen et al. (2012).

4.4. NH_3 and PM emissions from livestock farming (Papers IV and V)

Two measurement campaigns for the emission measurements from the loose housing cowshed were carried out, as milking cows are important NH_3 emitters in the livestock farming sector. In the first campaign (Paper IV) the main focus was to identify PM and NH_3 levels inside nine uninsulated loose housing cowsheds. In the second campaign (Paper V), the main focus was to identify the chemical composition of the different fractions of measured PM in the loose housing cowshed.

4.4.1. PM and NH_3 concentration measurements at the cowsheds (Paper IV)

Inhalable (PMtotal, PM_{10}), and respirable ($PM_{2.5}$, $PM_{1.0}$) particulate matter concentrations and NH_3 concentration ($\mu g/m^3$) as well as microclimate parameters (temperature [in degrees Celsius] and relative humidity [by percentage]) and CO_2 (ppm) were measured in nine large uninsulated loose housing cowsheds on five dairy production units in Estonia, once per month (Paper IV).

A Grimm 1.108 portable aerosol spectrometer (Grimm Technologies Inc., Aerosol Technik GmbH and Co) was used for the measurements of the concentrations of airborne particles (PMtotal, PM_{10}, $PM_{2.5}$, $PM_{1.0}$). A Dräger X-am 7000 multi-gas detector (Dräger Safety GmbH) was used to detect NH_3 (minimum detection limit 1 ppm) and CO_2 (minimum detection limit 300 ppm) gas concentrations inside the cowsheds. In all the buildings the temperature and relative humidity were constantly recorded at intervals of 15 min throughout the period of the experiment using a Rotronic HygroLog data logger (Rotronic AG). From the nearest monitoring station, PM_{10} and $PM_{2.5}$ regional background data was extracted and used for the background level estimation inside the cowsheds during the measurements (Paper IV).

From all cowsheds the 1-min mean concentrations of inhalable and respirable particles, CO_2 and NH_3 were measured at a 1 m height from

the floor, from 8 to 13 locations, depending on the size of the building, for a period of 10 min per measuring point. The total time period for sample collection ranged from 1.2 to 2.5 h per cowshed. Measurements were performed in the daytime, while the cows were most active and while different work routines (TMR feeding, manure removal) were being carried out. The indoor concentration of CO_2 provided the basis for indirect assessment of the effectiveness of the ventilation in the dairy buildings, i.e. lower CO_2 concentrations indicated a higher ventilation rate within the cowshed (Paper IV).

4.4.2. PM chemical composition measurements at the cowshed (Paper V)

Microclimate parameters and gas concentrations similar to Paper IV were measured, but in addition to that the fractional distribution of particulate matter (PM) mass ($\mu g/m^3$) and number ($1/cm^3$) concentrations (using an electrical low-pressure impactor, ELPI) were measured in an uninsulated loose housing cowshed in Märja, Estonia. The ELPI impactors cover the size range of 28 nm to 10.04 μm, with D50% aerodynamic cut points of 28 nm, 54 nm, 93 nm, 156 nm, 264 nm, 386 nm, 619 nm, 957 nm, 1.61 μm, 2.41 μm, 4.03 μm, 6.65 μm and 10.04 μm, respectively, for stages 1–13. For the PM mass calculations the particle average density of 1.68 g/cm^3 was assumed according to Cambra-López et al. (2011). At the particle inlet the DIGITEL Low Volume Inlet DPM1003 (1.8 m^3/h) was used for removing particles larger than 10 μm (aerodynamic size) and in addition Dekati® Dryer DD-600 Nafion® dryer was used to remove water from the aerosol before it enters the ELPI+. CO_2 concentration inside the cowshed was measured for the estimation of the ventilation rate (m^3/h). Measurement campaigns were carried out from 10/01/2010 to 12/02/2010 (representing winter period); from 18/03/2011 to 02/05/2011 (representing spring period); and from 01/02/2013 to 27/08/2013 (representing winter, spring and summer periods). These periods were chosen to have representative data for the cold and warm periods, as the concentrations of PM and NH_3 can vary according to the season. The one-minute average concentrations of PM, and CO_2 and three-second average concentrations of NH_3 were measured continuously during the whole campaign at a 2.5 metre height from the floor inside the barn. For NH_3 detection, the Picarro G2103 (Picarro Inc.) analyser was used, which uses a Wavelength-Scanned Cavity Ringdown Spectroscopy (WS-CRDS), with a range from 1 ppb to 50

ppm. For the CO_2 measurement a CARBOCAP GMT 222 (Vaisala Oy) with an infrared (IR) sensor was applied, with the minimum detection of 1 ppm. The temperature and relative humidity were determined in one-minute intervals with a HUMICAP HMT 130 data logger (Vaisala Oy). For the data collection and management, a Hydromet MAWS 110 (Vaisala Oy) system was used. Ionic composition of the particle fractions were analysed using ion chromatography (Dionex DX2000 and DX2100).

The background ambient air concentrations of PM_{10}, $PM_{2.5}$ and meteorological parameters were measured at the Saarejärve (58°43'39.44", 26°30'15.56") rural ambient air monitoring station (ca. 33 km north of the Märja cowshed). For the ambient PM_{10} and $PM_{2.5}$ measurements BAM 1020 (Met One Instruments Inc.) was applied, which measures ambient particulate concentration using beta ray attenuation with 1 h resolution from 1 to 1000 $\mu g/m^3$ (Paper V).

From the measured CO_2 concentration, the ventilation rate (V) was calculated using the equation developed by Pedersen et al. (1998). For the NH_3 background concentration the value 1.92 $\mu g/m^3$ from the Maasikmets (2007) study was applied, which was measured within 1 month during the summer period in the rural background near Tartu using a Radiello® passive sampler (Paper V).

4.5. Validation of the measured EF

In the current thesis the Tartu area was chosen to conduct the EF validation, where the combination of dispersion modelling and air quality data from the ambient monitoring network, was used. Tartu is the second largest city in Estonia with 97,332 inhabitants as of 2015 (Statistics Estonia, 2016). Tartu is situated in the post-glacial valley of the Emajõgi River, and the topography largely determines the conditions of pollutant distribution (Kimmel and Kaasik, 2003). The air quality in Tartu is influenced mostly by the traffic and residential heating emissions (Elser et al., 2016; Kaasik et al., 2001; Kimmel and Kaasik, 2003; Maasikmets et al., 2015a; Orru et al., 2011; Pindus et al., 2015; Saare et al., 2013; Vlachou et al., 2018) and also somewhat by nearby agricultural activities (Elser et al., 2018) (Paper IV and V). The industrial enterprises (food, timber production, building materials, etc.) are small and concentrated in a few areas (Kimmel and Kaasik, 2003). Industry (including boiler houses) has a low impact on the air quality of Tartu (Maasikmets et al., 2013; Orru

et al., 2009a), as nowadays heavy industry in Tartu is absent and central-heating boiler houses use flue gas cleaning measures like scrubbers and electrical precipitators. One-third of the people live in large (up to nine-storey) block houses (which use central-heating systems) located in the Annelinna neighbourhood. The second most populated area is the Karlova neighbourhood, which has many two- to three-storey apartment houses (Pindus et al., 2015) where the masonry heaters and stoves for heating and cooking purposes are widely used.

For the dispersion calculations, residential wood combustion (RWC), traffic non-exhaust, agricultural and industrial emission databases (EDB) were created including the location and emission rate (g/s for PM_{10} and $PM_{2.5}$ as well as NH_3 for livestock farming) for each emission source (Figure 3). The hourly mean concentrations from different sources were modelled in the Tartu area separately. $PM_{2.5}$ background concentrations were estimated using data from Saarejärve background monitoring station (located ca. 33 km north of Tartu). Thereafter the results were summed up and compared with the monitored results from the Tartu air quality monitoring station on Kalevi Street (Station 1) and from three other measurement locations (Figure 3).

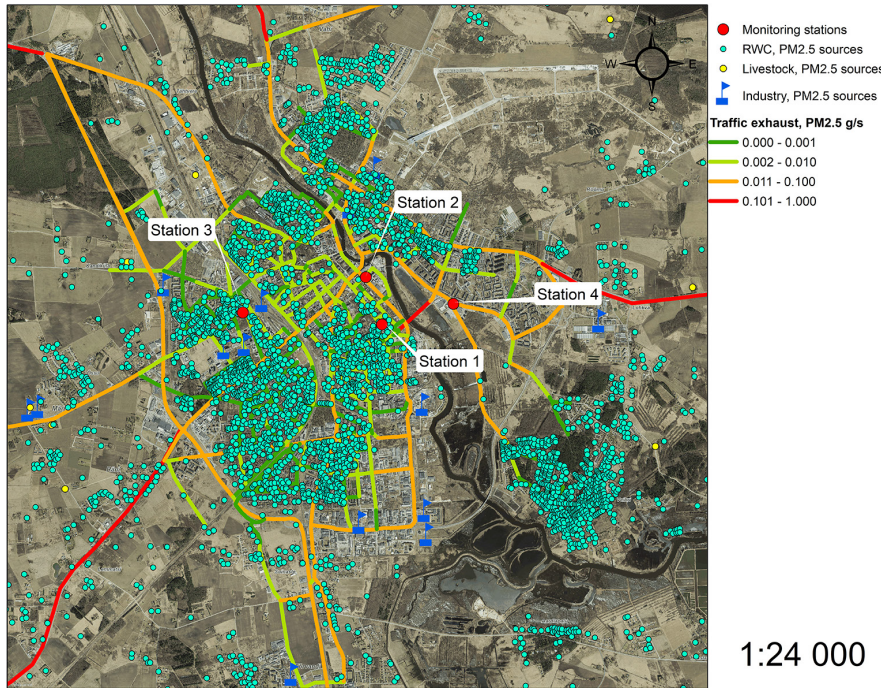

Figure 3. Location of emission sources and monitoring stations in Tartu in 2014

Hourly concentrations of $PM_{2.5}$ for January–May 2014 were modelled in 200 × 200 m grids all over the Tartu area with an Eulerian Advection-Diffusion grid dispersion model, which is the part of the Airviro Air Quality Management System. A detailed description of the model is given in the Airviro User Documentation (Apertum, 2018a). Airviro (Apertum IT, Sweden and EERC, Estonia) is a web-based air pollution data management tool that uses data on air emissions, measured levels of air pollution from monitoring stations and meteorological variables from meteorological stations. Airviro is a widely used system for dispersion calculations and air quality assessments (Johansson and Eneroth, 2007; Johansson et al., 2017; Khan et al., 2018; Klepac et al., 2018; Maasikmets et al., 2013; Orru et al., 2011; Shekarrizfard et al., 2018).

For the RWC EDB, data from the construction registry (living area in m^2 and heating system) and cadastral registry (cadastral location) was used, which allows to locate each household, using wood for heating, with location precision of cadastral unit. For each household $PM_{2.5}$ emission (g/s) was calculated, according to the household living area size (m^2). The RWC emission database was based on EF which were measured in the Estonian Environmental Research Centre stove testing laboratory (Maasikmets et al., 2015b; Teinemaa et al., 2013) (Figure 4) in combination with Paper II. The average energy consumption of 242 kWh/m^2/a per household was assumed (Loosaar et al., 2008). Weighted emission factor for $PM_{2.5}$ was calculated, assuming that 65% of the households use a newer type of heaters (with a grate inside the heater and advanced stoves for the local central heating) and 35% of the households use an older type (without a grate and the heater door used for oxygen intake) of stoves and/or heaters (Maasikmets et al., 2015b). Based on the expert estimation of Dr. M. Kaasik, it was assumed that 23% of the households use unknown heating systems (most probably local central heating stoves) and 77% use different kind of stoves and heaters. Those assumptions were taken into account in the Estonian air pollutants emission inventory (EEEA, 2018a).

As ambient air measurements in Tartu indicate (Elser et al., 2016; Kupri et al., 2018; Maasikmets et al., 2015a; Vlachou et al., 2018), besides pure wood some MSW is also burned in stoves and heaters, and it is important to take this factor into account. However, it is difficult to assess the exact quantity of burned waste and the exact number of households which practice this bad habit. Within this thesis, calculations with two scenarios

were performed. In the first set-up (45% MSW scenario, around 800 Tonnes of burnable municipal waste is burned annually in Tartu) we have assumed that 45% of the population burns some household waste, like plastic and Tetra packages, as used in Estonian official air pollutants emission inventory (EEEA, 2018a). In the second set-up (2% MSW scenario, around 35 Tonnes of burnable municipal waste is burned annually in Tartu) it has been assumed that a maximum of 2% of the population does it regularly (NIR, 2018). Calculated EF for $PM_{2.5}$ for two scenarios are shown in Figure 5. Using the total yearly energy consumption, $PM_{2.5}$ emission (g/s) for each household was calculated, in total for around 12,700 sources in the Tartu area.

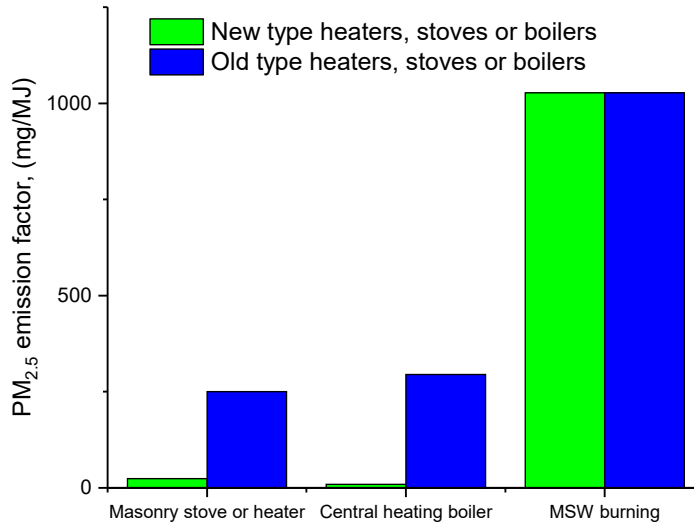

Figure 4. EF used for the weighted $PM_{2.5}$ EF

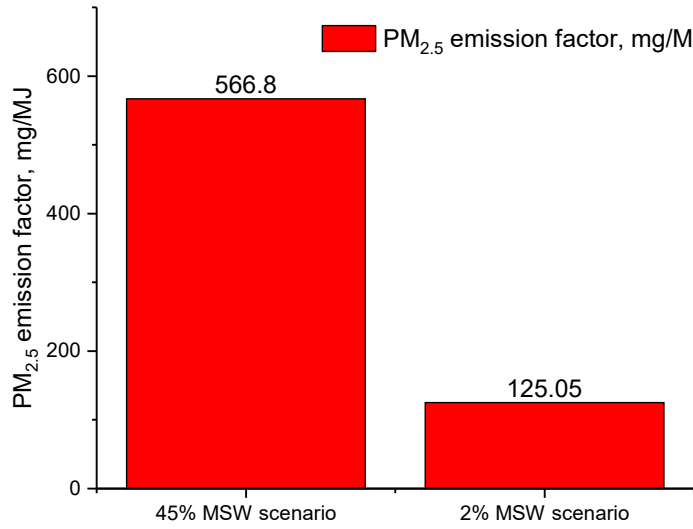

Figure 5. Weighted $PM_{2.5}$ EF for 2% and 45% MSW scenario

For the diurnal hourly dynamics of the RWC emissions and yearly cycle, equivalent black carbon (eBC) measurements (Figure 6 and Figure 7) were used, based on measurements conducted at the Kalevi Street monitoring station using an aethalometer (Magee Scientific, AE-33). AE-33 measures the aerosol light absorption and determines the eBC concentrations in seven different wavelengths (370, 470, 520, 590, 660, 880, and 950 nm), which covers the range between ultraviolet and infrared and allows for the source apportionment of different eBC fractions (Zotter, 2015). AE-33 can be used to separate eBC from wood burning (eBC_{bb}) and from traffic (eBC_{ff}), by taking advantage of the spectral dependence of absorption, described by the Ångström exponent (Drinovec et al., 2015; Sandradewi et al., 2008; Zotter et al., 2016). In this study an Ångström exponent of 0.9 for traffic and 1.7 for wood burning were used similar to previous studies (Elser et al., 2016). For the estimation of biomass emission related dynamics and strength eBC_{bb} concentration as the proxy was used.

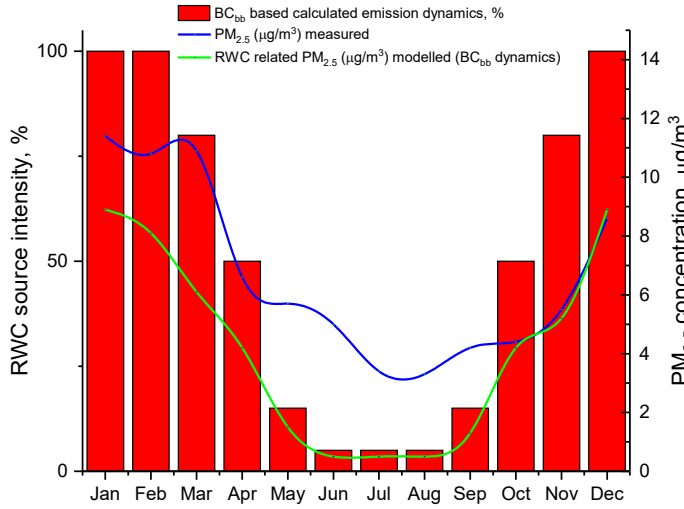

Figure 6. Monthly dynamic in RWC EDB

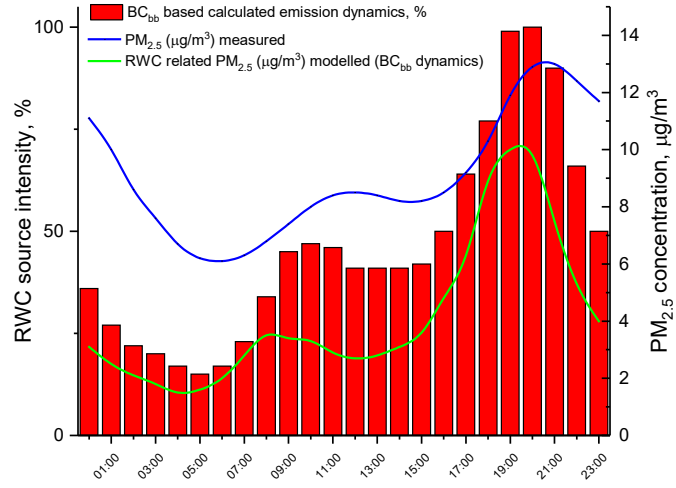

Figure 7. Diurnal dynamic in RWC EDB

Traffic EDB was based on traffic counting (2011) and for the exhaust emission EEA/Corinair EF (EEA, 2013) were used. A road source is a mathematical idealisation that does not exist in reality, as every car moving on the road is more or less a point source, although we can never locate or follow any individual car. The road as line source is with the fixed position, where in addition to that information on traffic speed, traffic intensity and variation as well as information on the types and

proportions of vehicles operating on that road are needed (Apertum, 2018b). A more detailed overview about the traffic EDB inputs and functionality can be found in Apertum (2018b).

For the non-exhaust EF validation studded tyre PM_{10} EF (in order to see the maximum possible impact) from the Paper III was used and the Gaussian resuspension model according to Omstedt et al. (2005) in Airviro modelling system was applied. Resuspension EDB uses same input like traffic EDB, but in addition data about sanding/salting and various meteorological parameters are used, in order to estimate the time intervals when the PM loading from the road surface is emitted. As exact data about salting and possible sanding for Tartu was absent, the daily average temperatures were used to assess these activities. In addition, for model input the following assumptions were made:

1. In winter, the average proportions of studded and non-studded tyres in Estonia are 76.2% and 23.8%, respectively (Koppel et al., 2005).
2. Winter tyres are used for 210 and summer tyres for 155 days per year, in order to simulate a worst-case scenario.
3. On average there are 121 days annually with rainfall ($\geq$ 1.0 mm) and the average number of days with snow is 109 (EMHI, 2014).

For the agricultural EDB data from the Estonian Agricultural and Information Agency (EAIA) was used. In 2015 there were around 6,000 households where goats, sheep, pigs or cattle are raised. EDB includes data about all facilities and farms that are known to have at least one animal, including the number of animals by animal group (cattle, pigs, sheep, goats and poultry), address, coordinates and number of registry. Using Paper IV and V results, PM_{10}, $PM_{2.5}$ and NH_3 emissions were calculated per facility using a similar approach to the one described by Oravas (2015).

Modelled results were compared and validated with the $PM_{2.5}$ and $PM_{1.0}$ results measured at the Kalevi monitoring station and during the heating season campaign (January–May 2014) as well as at other monitoring stations (Figure 3). $PM_{2.5}$ 1-hour mass concentrations ($\mu g/m^3$) were measured with beta-attenuation method (BAM-1020, Met One Instruments Inc.).

In addition, online non-refractory submicron particles (NR-$PM_{1.0}$) and its chemical composition, for the validation of the modelled RWC share from the total PM mass concentration, were used. An Aerosol Chemical Speciation Monitor (Q-ACSM, Aerodyne Research Inc.) has been running at the Kalevi Street monitoring station since June 2014. The Q-ACSM is based on the widely used Aerodyne Aerosol Mass Spectrometer (AMS) technique and combines an aerodynamic lens for particle focusing with high-vacuum particle thermal vaporization, electron impact ionization, and mass spectrometry (Ng et al., 2011b). The Q-ACSM measures non-refractory $PM_{1.0}$ chemical composition (organics, SO_4, NO_3, NH_4 and Chl) with a time resolution of ca. 30 min using a quadrupole mass-spectrometer. In order to account for the particle losses in the vaporizer, a composition dependent collection efficiency (CDCE) according to Middlebrook et al. (2012) was calculated and the mean CDCE from December 2016 to May 2017 was 0.62 ± 0.15, which is slightly higher than the commonly used default CDCE of 0.5. During the measurement period the Q-ACSM relative ionization efficiency (RIE) for ammonium and sulfate was 6.13 and 0.58, respectively, and the response factor (RF) for nitrate was $4.65e^{-11}$. The organic aerosol fraction was analysed by applying a multilinear engine algorithm (ME-2) for organic mass spectra in order to explain the main sources of OA in the Tartu area using SoFi 6.61 software (Canonaco et al., 2013) for the 2016/17 heating season (December 2016–May 2017) data.

By using the source apportionment method, organic aerosols can be divided into factors representing different particle sources like traffic (hydrocarbon-like organic aerosol, HOA, which is mostly related to traffic), biomass burning (BBOA) and cooking (COA), or into factors that represent components with similar chemical characters, such as low-volatility (LV) and semi-volatile (SV) oxygenated organic aerosol (OOA) (Aurela et al., 2015). The number of factors was selected based on the unexplained variation, changes in the Q-value (the total sum of the squares of the scaled residuals), the comparison of mass spectra with the AMS mass spectra database (Ng et al., 2011a) and/or by using species such as BC, inorganic ions, NO_x and meteorological data (Canonaco et al., 2013; Crippa et al., 2013).

During the first run all factors were kept unconstrained to see whether factors could be distinguished in unconstrained mode and as reference profiles for HOA, BBOA and COA from Crippa et al. (2013) and Ng et

al. (2011a) were used. Later HOA and COA factor profiles and time series were constrained according to references by Crippa et al. (2013), where the HOA and COA reference spectra was taken from the measurements in Paris. All other factors were separated by using the unconstrained method. An HOA and COA mass spectrum was used as an input data with an α-value of 0.4. The α -value determines the extent to which the output is allowed to vary from the input, i.e. an α-value of 0.4 means that the contributions of the mass spectral ions concentrations are allowed to vary up to 40% and α-values in a range of 0–0.5 were tested to find the most reasonable one. The Q-ACSM dataset was separated into three two-month periods (Dec–Jan, Feb–March, Apr–May) and for each period up to 50 runs were made and the results with the highest correlations with tracers were selected.

5. RESULTS

5.1. Health impacts (Paper I)

The city centres and neighbourhoods with local heating could be clearly distinguished as areas with bigger exposure to fine particles. Higher concentrations also appeared in residential areas close to busy streets. The lowest levels appeared in residential areas at the edge of the cities, where population density is relatively low, e.g. the levels in Ihaste neighbourhood in Tartu was in average 7.6 $\mu g/m^3$. The daily averages of PM_{10} differed considerably among days and cities. The majority of the PM_{10} daily levels stayed between 10 and 30 $\mu g/m^3$.

The modelling results were validated with monitoring station data in all cities. The average difference for all monitoring stations above modelled PM levels over measurements time was 22%. In Tartu, the modelled levels were mainly higher than the measured levels. This shows that the emission databases for local heating have probably been overestimated. Even the agreements between the measured and modelled PM levels were imperfect; the model should satisfactorily represent the particle levels at different receptor points in the city as well.

Altogether it was possible to define 650,225 inhabitants in five cities, 101,192 of them in Tartu.

The exposure to fine particles could cause on average of 462 premature deaths per year, corresponding to 6,034 YLL. This is likely to be reflected in the reduction of life expectancy by an average of 0.64 years in Tallinn, 0.68 years in Tartu and 0.95 years in Pärnu. In the city centres and in regions with extensive local heating, the life expectancy may be decreased by up to 1.2 years, whereas in the least polluted neighbourhoods the decrease of life expectancy remains around 0.3 years. If the average number of YLL is divided by the number of premature deaths, the loss will be approximately 13 years among these persons. This indicates greater health impacts among certain risk groups. These risk groups include people with chronic respiratory and cardiovascular disease and immunosuppressed persons who could live several years less due to outdoor air pollution exposure. Additionally, 231 (95% CI 145–306)

respiratory and 338 (95% CI 205–454) cardiovascular hospitalizations could be expected annually due to short-term exposure to PM_{10}.

We assessed that most of the external costs of air pollution are related to the long-term effects on mortality and years of life lost due to premature deaths. Annually, this imposes a cost of up to €270 million (95% CI 190–350). Compared to losses from premature mortality, the costs of short-term exposure are small: €1.1 million (95% CI 0.6–1.6). A majority of the latter (> 55%) are directly related to hospitalizations and the rest to lost input to the national economy due to time spent on sick leave.

5.2. Wood and MSW burning emissions from residential heating appliances (Paper II)

Most of the wood burning EF in residential sector do not take into account the share of MSW added during the heating process; therefore, measured EF might not be representative of the local circumstances. In order to develop country-specific EF for Estonia, it is important to include MSW burning share from the residential sector as well, as ambient air measurements indicate that some MSW is burned in household heating appliances.

During the simulation of wood and MSW burning experiments in the laboratory scale, the mean $PM_{2.5}$ concentration was 929.5 (95% CI 560.7–1298.2) mg/Nm^3 (13% O_2). The highest concentrations were measured during year 2000 experiments, with the mean level of 2,336.8 (95% CI 605.7–4,067.8) mg/Nm^3 (13% O_2). High concentrations were caused mostly by the high load of MSW and a rapid concentration increase during the fuel adding was observed (Paper II).

During our experiments, it was noted that particle number (PN), HCl, and CO_2 concentrations rose during the fuel adding process and CH_4 level rose during the mixing of fuels (Paper II, Supporting Material, Fig. S1).

We saw that PM emission and size distribution from heaters largely depends on combustion conditions (Paper II, Supporting Material, Fig. S1), which is mainly caused by incomplete combustion due to excessively fast pyrolysis and increased ash release due to a high combustion temperature. It was also observed that during the firing phase and after

adding fuel, the PM size distribution changed to a slightly bigger size fraction (Paper II, Supporting material, Fig. S2). We noticed a remarkable increase of PM and PN concentrations during the firing phase and fuel adding (Paper II), in line with findings of Tissari et al. (2009).

Regarding the toxic compounds like PCDD/F, we found that during some experiments the mean levels of PCDD/F (0.0116–0.1550 ng I-TEQ Nm^3 11% O_2) were higher than the legal limit value for combustion of MSW in waste incineration plants, which is PCDD/F 0.1 ng I-TEQ Nm^3 (11% O_2) (IED, 2010).

Based on measured $PM_{2.5}$ concentrations EF were calculated and the results are shown in Figure 8 (Wood + MSW) in comparison with other results (EEA, 2013; Maasikmets et al., 2015b; Teinemaa et al., 2013).

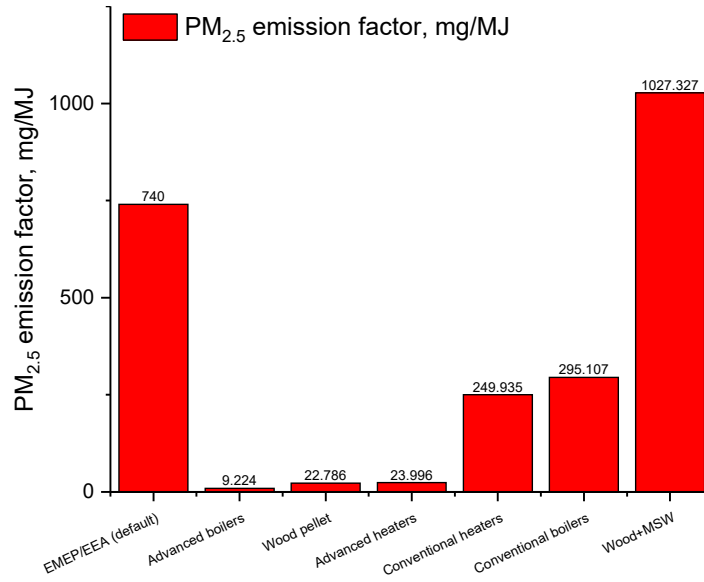

Figure 8. $PM_{2.5}$ emission factors (mg/MJ) from Paper II and other studies

5.3. Non-exhaust emissions (Paper III)

Our results show that the PM_{10} EF is the greatest with studded tyres, at speeds both below and above 50 km/h. Moreover, there was a correlation between PM_{10} mass concentration and vehicle speed in the summer tyre test (Figure 9). This trend is consistent with earlier studies (Mathissen et

al., 2012; Pirjola et al., 2009). The higher emissions are predominantly caused by the greater abrasion of road surfaces by studded tyres, and the studs' own wear in this process. Higher EF of non-studded (friction) tyres in comparison with summer tyres, is primarily caused by their softer material (Paper III).

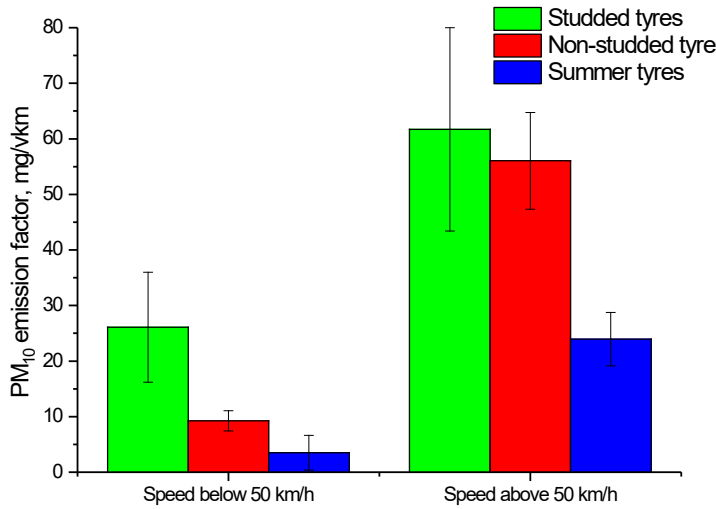

Figure 9. PM_{10} EF dependency from vehicle speed and tyre type (Paper III)

The mean PM_{10} EF of non-studded tyres was 32.6 ± 5.3 mg/vkm, which is comparable to published data of 26 ± 19 mg/vkm (Mathissen et al., 2012) and 30 ± 14 mg/vkm (Bukowiecki et al., 2010). Estonia has used until now PM_{10} EF for cars derived from the official EEA/ Corinair guidebook (EEA, 2016), where EF depends on the car type: passengers cars 7.5 mg/vkm, light-duty vehicles (LDV) 7.5 mg/vkm and heavy-duty vehicles (HDV) 38 mg/vkm, which gives in average PM_{10} EF of 17.7 mg/vkm, which is somewhat lower than our > 50 km/h results, but comparable to our < 50 km/h results. To compare our EF to countries with similar conditions regarding the studded tyre usage, Finland, for example, uses in official emission inventory PM_{10} EF 56.9 mg/vkm and Sweden uses EF 32.8 mg/vkm, which includes emissions from road abrasion, brake and tyre wear and also takes into account the share of studded tyres (Denier van der Gon et al., 2018).

It was noticed that during the tests the largest mass concentration of particles is produced in the coarser particle size fraction, varying somewhat depending on the tyre type. Studded tyres produce a somewhat greater

proportion of coarser particles when compared to non-studded and summer tyres, while the particle size with the highest mass concentration is around 8 μm for both the non-studded and studded tyres (Paper III).

Our tests with summer tyres showed that vehicle speed affects tyre temperature (Paper III, Figure 6), but there was no correlation between any measured particulate fraction and tyre temperature. Between vehicle speed and tyre temperature there was a moderate polynomial correlation ($R^2 = 0.51$). The tyre temperature rose rapidly at the beginning of the ride from 27°C up to 35°C and after that the heating process continued more slowly. At the end of the test (180 km highway with 100 km/h speed limit, driving time 2 hours 30 minutes) the tyre temperature rose up to 42°C. During the test the ambient temperature ranged between 22°C and 27°C (Paper III).

Test measurements showed that losses in the measurement system ranged from 2.4% ($PM_{1.0}$) to 46% (PM_{10}). Sampling losses may be expected to be greater for coarser particles, leading to an underestimation of coarse particle emissions; therefore possible PM losses were taken into account (Paper III).

The results show that higher vehicle speeds produce larger amounts of non-exhaust emissions. Particulate EF depends on tyre type - winter tyres produce more coarse particulates (Paper III). These results are consistent with earlier studies (Hussein et al., 2008; Mathissen et al., 2012; Pirjola et al., 2009).

5.4. PM and NH_3 emissions from livestock farming (Papers IV and V)

There was a clear seasonal variation in measured indoor concentrations between the warmer and colder periods. In the warmer period (from May to September) the concentration of the different PM fractions, CO_2 and relative humidity inside the uninsulated loose housing cattle buildings was lower than in the colder period. However, we observed that the temperatures and the NH_3 concentrations were higher during the warmer period. Also, the variation within the months of the warmer period was smaller than in the colder period (Papers IV, V).

The daily mean $PM_{2.5}$ and PM_{10} emission were 0.19 ± 0.33 and 0.36 ± 0.48 per livestock unit in grams (g LU^{-1} d^{-1}), respectively. PM emissions were higher during the colder period and lowest for $PM_{2.5}$ during the warmer period. For PM_{10} it was lowest during the spring period. Schrade et al. (2014) observed PM_{10} emissions in the range of 0.02 and 2.1 g LU^{-1} d^{-1}, which are generally comparable to our results. During the spring period, the highest $PM_{2.5}$ and PM_{10} background values were observed, which is normal in Estonia because the heating season is still ongoing, and additionally after snow melt PM emissions from resuspension occur (Paper V).

The PM ionic composition from ELPI filters was analysed (Figure 10). PM levels in the cowshed were more influenced during the winter and spring seasons by other sources, like residential wood combustion (elevated K^+) and regional pollution (elevated SO_4^{2-} levels). Elevated NH_4^+ levels during winter can be caused by the local farm itself or by regional pollution, because of low temperatures or high relative humidity and the presence of NH_3 (Paper V).

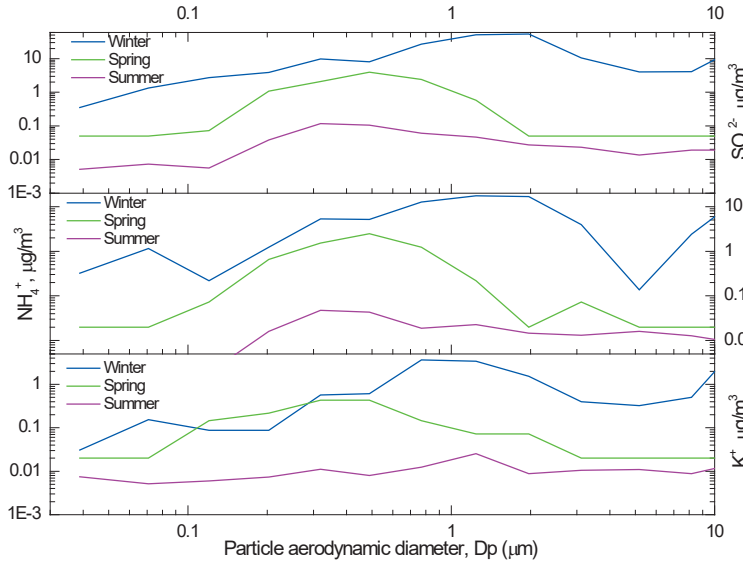

Figure 10. PM ionic composition of ELPI filters during different seasons (Paper V)

On average, the ventilation rate was 260.6 ± 12.1 m^3 h^{-1} per LU and the highest ventilation rate occurred during the spring time, which is comparable with other results (Ruus, 2013; Seedorf et al., 1998).

5.5. Validation of emission factors

For the air quality modelling, the period from 01/01/2014 to 30/04/2014 was chosen, as during that period an intensive measurement campaign in four different places was carried out, using one stationary measurement container (Station 1) on Kalevi Street and three mobile measurement stations in stationary mode (Stations 2, 3 and 4). In addition period from 06/12/2016 to 05/05/2017 and 01/01/2017 to 01/01/2018 for the validation was chosen, in order to compare modelled and measured results in Station 1. In this thesis the main focus is to assess whether the measured EF are in line with real ambient measurements. In addition, the dispersion modelling technique has been employed in order to identify whether the modelled and monitored $PM_{2.5}$ results are comparable, thus showing how well the measured EF are representative of the real-world situation.

For the modelling purpose, livestock farming, traffic exhaust (not including non-exhaust emissions as they are mostly of coarser mode), industrial and residential wood combustion sectors were modelled separately and later summed up. The regional $PM_{2.5}$ background level from the Saarejärve background monitoring station (ca. 33 km north of Tartu) was taken into account.

Using a 2% MSW scenario (EF of RWC $PM_{2.5}$=125.05 mg/MJ) in the RWC sector, the modelled values at Stations 2 and 4 were lower and at Stations 1 and 3, conversely, they were higher (Figure 11). The 45% MSW scenario (EF of RWC $PM_{2.5}$ = 566.80 mg/MJ) approach gave higher modelled results in all monitoring stations, except Station 4, where higher $PM_{2.5}$ values were measured in comparison with the modelling results.

The average modelled $PM_{2.5}$ concentration in monitoring stations ranged from 11.8 to 13.6 $\mu g/m^3$ for the 2% MSW scenario, being highest at Station 2, which was located at Turu Street 6 next to the gasoline station and a busy street. For the 45% MSW scenario, the modelled results ranged from 15.8 to 26.5 $\mu g/m^3$, being highest at Station 3, which was located in Puusepa Street near Maarjamõisa kindergarten.

Modelled wood and MSW share from the total $PM_{2.5}$ concentration ranged from 1.1 to 4.0 $\mu g/m^3$ for 2% MSW scenario and from 5.0 to 18.2 $\mu g/m^3$, being highest in both cases in Station 3.

Measured $PM_{2.5}$ concentrations ranged from 10.3 to 19.2 μg/m^3, being highest at Station 4 and lowest at Station 1 (Kalevi monitoring station).

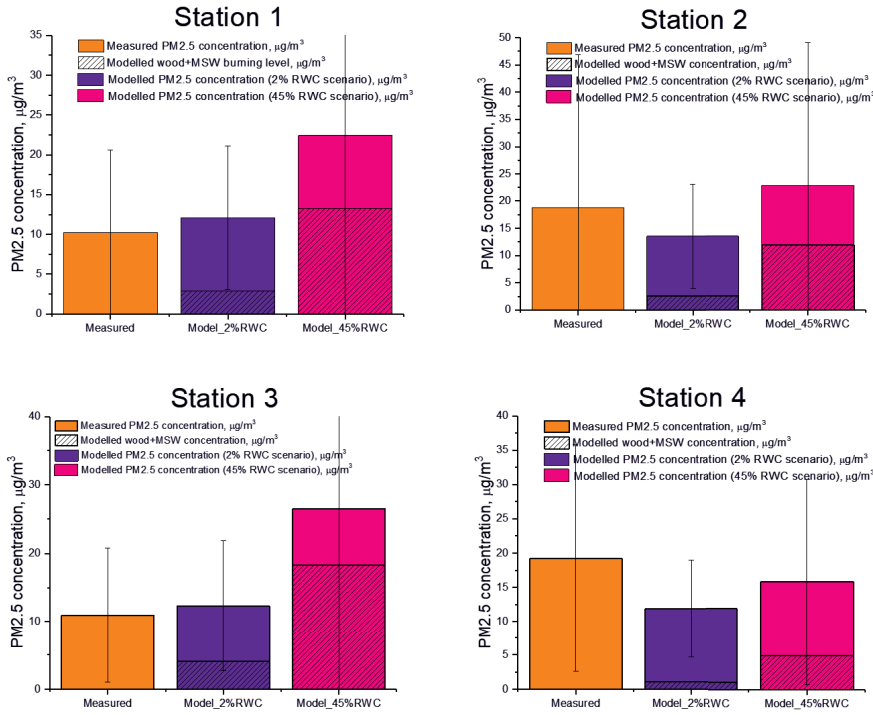

Figure 11. Average measured and modelled $PM_{2.5}$ concentrations in monitoring stations in January–April 2014

Air quality modelling was used for the Tartu city area and it can be seen that highest modelled results have occurred in the city centre and in the Riia Street area (highest concentrations near Cinema Ekraan), where the modelled results range from 16 to 32 μg/m^3 for 2% MSW and 45% MSW scenarios, respectively (Figure 12 and Figure 13).

In general, a good agreement with the 2% MSW scenario and monitored results was found, where a good correlation ($r > 0.500$) between measured and modelled $PM_{2.5}$ values at Stations 1, 2 and 4 was observed (Table 1). The 45% MSW scenario mostly overestimated $PM_{2.5}$ concentrations in all monitoring stations and also had a somewhat weaker correlation between measured and modelled values.

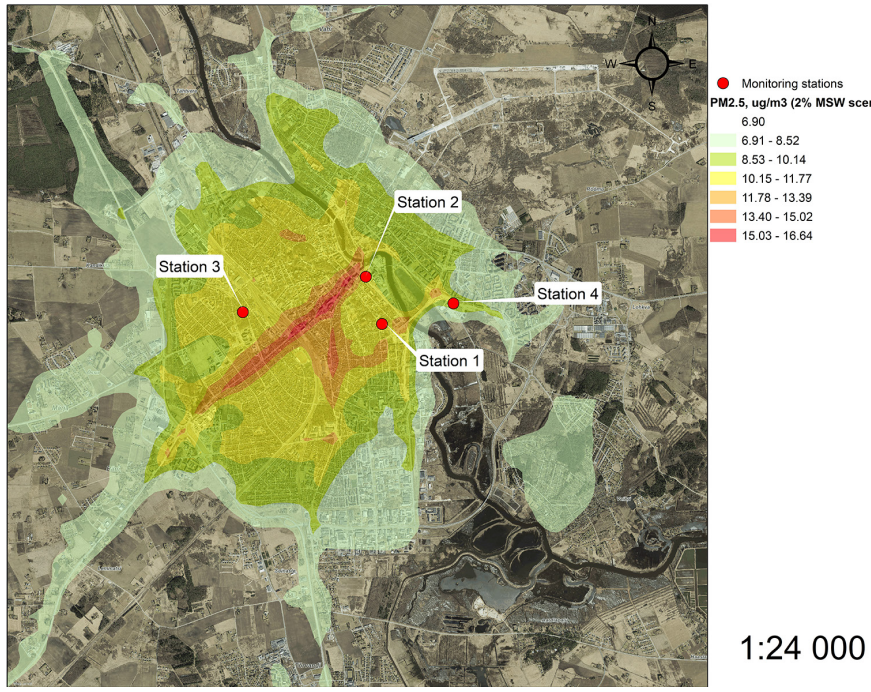

Figure 12. Modelled average $PM_{2.5}$ concentrations in Tartu area (2% MSW scenario, January–April 2014)

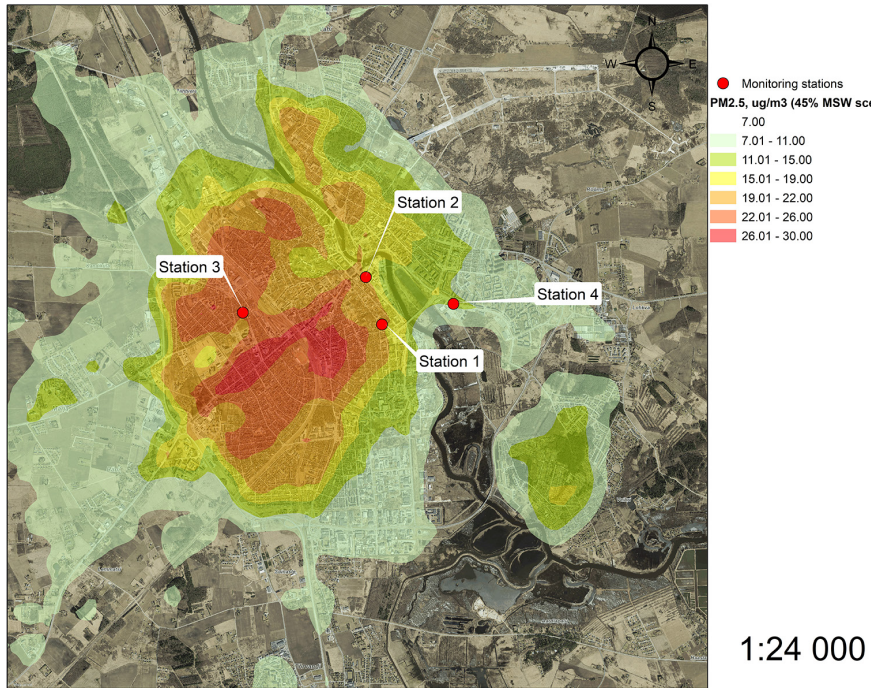

Figure 13. Modelled average $PM_{2.5}$ concentrations in Tartu area (45% MSW scenario, January–April 2014)

Table 1. Correlation coefficients between measured and modelled $PM_{2.5}$ values in monitoring stations during 2014 campaign

Station, measured	Modelled scenario	Correlation coefficient r
Station 1	2% MSW scenario	0.609
	45% MSW scenario	0.503
Station 2	2% MSW scenario	0.312
	45% MSW scenario	0.331
Station 3	2% MSW scenario	0.690
	45% MSW scenario	0.623
Station 4	2% MSW scenario	0.575
	45% MSW scenario	0.518

During the 2016/17 heating season campaign, in source apportionment analysis five main factors (Figure 14) at Station 1 were identified. According to the mass-to-charge (m/z) ratio, we could see: biomass burning aerosols (BBOA, main m/z markers 29, 60, 73), hydrocarbon-like organic aerosols (HOA, main m/z markers 27, 41, 43, 44, 55, 57, 69, 71, mostly related to traffic exhaust emissions), cooking organic aerosols (COA, main m/z markers 44, 55, 57, 98), semi-volatile oxidized organic aerosols (SV-OOA, correlation with ammonium nitrate) and low-volatile oxidized organic aerosol (LV-OOA, correlation with sulfate).

The mean concentrations of NR-$PM_{1.0}$, calculated by summing up all chemical species measured by the Q-ACSM (organics, nitrate, sulphate, ammonium, chloride), was 4.63 ± 4.35 $\mu g/m^3$ (Table 2).

Table 2. The concentrations (mean ± STDEV) in μg/m^3 (2016–2017 heating season)

Parameter	Station 1
$PM_{2.5}$	9.30 ± 9.21
eBC	2.00 ± 2.66
eBC_{bb}	1.38 ± 2.05
eBC_{ff}	0.62 ± 0.91
NR-$PM_{1.0}$	4.63 ± 4.35
organics	2.84 ± 3.16
sulfate	0.81 ± 0.81
nitrate	0.62 ± 0.70
ammonium	0.29 ± 0.30
chloride	0.07 ± 0.08

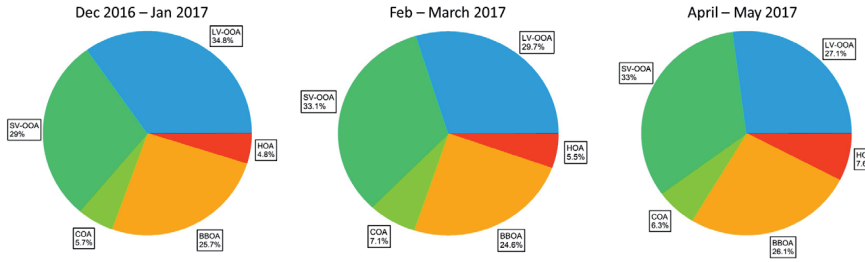

Figure 14. Relative contribution of OA factors (during 2016–2017 heating season, Dec 2016 - Jan 2017 – BBOA 25.7%, HOA 4.8%, COA 5.7%, SV-OOA 29%, LV-OOA 34.8%; Feb – March 2017 – BBOA 24.6%, HOA 5.5%, COA 7.1%, SV-OOA 33.1%, LV-OOA 29.7%; April – May 2017 – BBOA 26.1%, HOA 7.6%. COA 6.3%, SV-OOA 33%, LV-OOA 27.1%)

The air quality modelling approach with two RWC scenarios was used for the same period. It can also be seen that in this case the 45% MSW scenario largely overestimates $PM_{2.5}$ concentrations in comparison with measured $PM_{2.5}$ values (Figure 15). The 2% MSW scenario was in good agreement with measured and modelled values and had strong correlation (r = 0.637) with measured values.

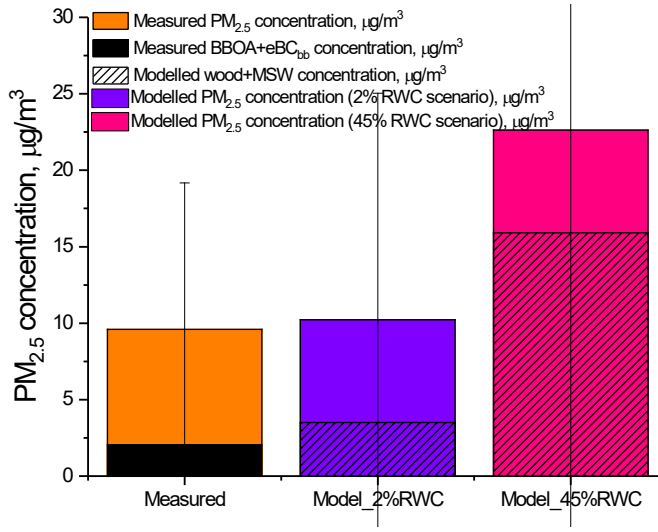

Figure 15. Mean measured and modelled $PM_{2.5}$ concentrations in Kalevi monitoring station during 2016–2017 heating season

Next the measured (eBC_{bb} and $PM_{2.5}$) and modelled (2% MSW scenario with RWC share and sum of all sectors) data from 01/01/2017 to 01/01/2018 from Station 1 was compared, to identify patterns of modelled and measured results during the whole year cycle. Between the measured and modelled $PM_{2.5}$ (Figure 16) a good correlation ($r = 0.702$) during the 2017 period at Station 1 was found and yearly mean concentrations are 7.3 ± 5.3 and 8.2 ± 5.1 µg/m^3, respectively, for the measured and modelled results.

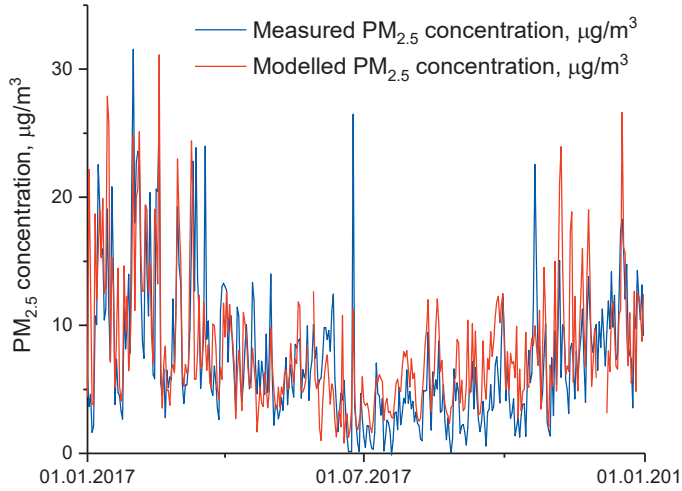

Figure 16. Measured $PM_{2.5}$ and modelled $PM_{2.5}$ (all sectors 2% MSW scenario + background) daily mean concentrations, µg/m^3 (2017)

Figure 17 shows yearly mean concentrations during 2017 of measured and modelled results at Station 1, including eBC_{bb} and eBC_{ff} share from the measured $PM_{2.5}$ concentration and modelled source apportionment of $PM_{2.5}$. Modelled yearly average $PM_{2.5}$ concentrations were around 12% higher than measured $PM_{2.5}$ concentrations.

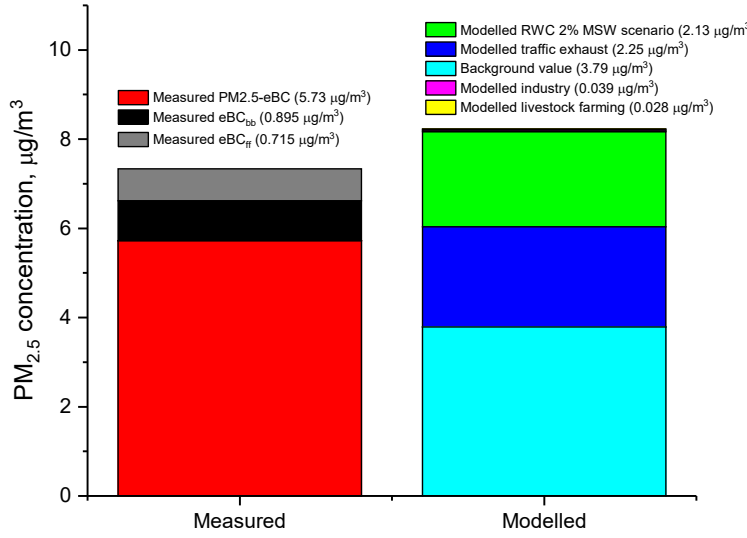

Figure 17. Measured $PM_{2.5}$, eBC and modelled $PM_{2.5}$ (all sectors separately + background) yearly mean concentrations (μg/m^3 in 2017 at Station 1)

As non-exhaust emissions contribute most to coarse particle ($PM_{2.5–10}$) emissions, the measured $PM_{2.5–10}$ data from Station 1 (Kalevi Street monitoring station) was compared against the modelled $PM_{2.5–10}$ concentrations throughout the whole year (2014) (Figure 18). The first run was performed using the measured EF (64 mg/vkm, Paper III) and in a later run the higher EF (460 mg/vkm) value was used. The results show that both modelled results (with lower and higher EF) do not follow the measured $PM_{2.5–10}$ trend and large discrepancies can be seen. Especially during the spring period, when the highest $PM_{2.5–10}$ concentrations have been measured, the model does not predict it correctly (Figure 18). Using lower EF, the results are largely underestimated and when using higher EF, the model overestimates the results during the autumn period.

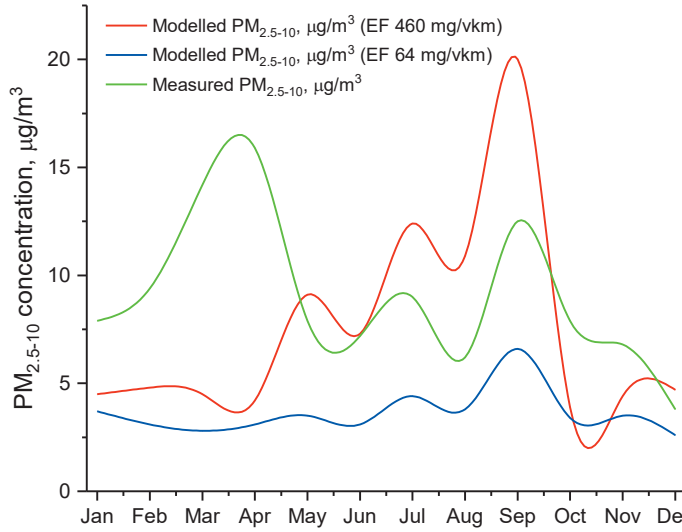

Figure 18. Measured and modelled non-exhaust $PM_{2.5–10}$ concentrations

As livestock farming's direct effect on PM emissions in Tartu is difficult to identify, mostly due to possible secondary origins, measured EF were used to calculate the total national PM and NH_3 emissions and compared with the official emission inventory values. According to the Estonian national emission inventory, 100,000 dairy cows emit 3.33 (with manure storage), 0.023, and 0.035 kilotons (kt) of NH_3, $PM_{2.5}$, and PM_{10} per year, respectively in 2015. The calculated yearly emissions for 100,000 dairy cows according to the measured average EF: yearly emissions of NH_3 (without manure storage, the share of which is around 50%), $PM_{2.5}$ and PM_{10} are 1.82, 0.019 and 0.036 kt, respectively, which is the same order of magnitude reported by the official inventory using default EF from EEA (2013). Dairy NH_3, $PM_{2.5}$, and PM_{10} yearly emissions contributed, respectively, around 16%, 0.1%, and 0.14% to the total Estonian yearly emissions, which shows that direct PM emissions from the dairy cowsheds are negligible, but NH_3 emissions contribute a remarkable amount to the total NH_3 emission.

In order to see the possible direct NH_3 contribution of agriculture and traffic emissions on NH_3 levels in the city centre, in spring 2014 (March–April) NH_3 levels near Circle-K (former Statoil) gasoline station on Turu Street 6 were measured using Picarro G2401 in a mobile measurement van MARU (Station 2). The measurements showed that NH_3 concentrations in the city centre are rather high (3.05 ± 1.56 µg/m^3),

but do not always follow the same daily cycle as NO_2 concentrations measured in the same position (Figure 19). Measured NH_3 levels are higher than normally measured in background stations (in Lahemaa the yearly average is around 0.2 μg/m^3), but as the Pearson correlation coefficient between measured NO_2 and NH_3 is moderate (r = 0.42), it can be assumed that besides traffic sources there might be some other important emission sources that influence NH_3 levels in the city centre. Thus it can be assumed that regional and local sources (including fuel burning and agricultural activities) might also have an effect on Tartu's air quality regarding NH_3 levels, which is in line with findings by Elser et al. (2018), where traffic-related NH_3 enhancement in Tartu was 38.3%.

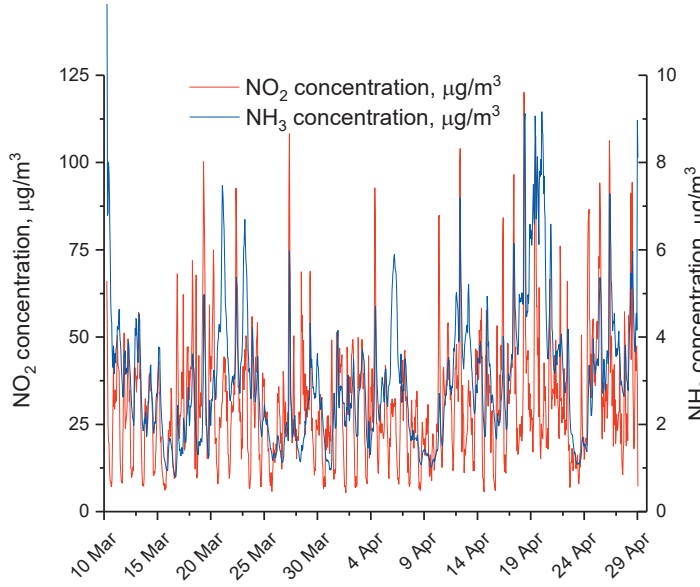

Figure 19. NO_2 and NH_3 concentrations in Station 2 (Tartu Turu Street in March–May 2014)

6. DISCUSSION

Despite the relatively clean air in Estonia, air pollution poses significant risks to public health. In residential heating areas in Northern Europe and Estonia, a majority of private households have their own heating system, each of which is a source of pollutant emissions. In addition, traffic is increasing in major Estonian cities, which, despite decreasing EF, contributes largely to air pollution emissions (Elser et al., 2016; Stratum, 2017). Moreover, the EF might differ in real-world conditions (Franco et al., 2013) and the non-exhaust emissions stay high or even increase with increased traffic volumes (Amato et al., 2014). From the source apportionment study carried out within this thesis and from previous studies (Elser et al., 2016; Maasikmets et al., 2015a; Vlachou et al., 2018), it can be seen that secondary aerosols may contribute around 30%–60% of the total NR-$PM_{1.0}$ in Tartu. This is important to take into account when air quality impact studies and/or emission reduction measures at the local level are planned. Livestock farming did not show any significant direct effect on Tartu air quality regarding primary PM emissions, but it can be assumed that livestock farming influences air quality in cities through secondary particle formation processes (Bauer et al., 2016; Sun et al., 2017). Thus further research regarding this topic is needed.

6.1. Health relevance

Particulate air pollution health impact assessments in the five main Estonian cities showed that fine PM in ambient air could shorten life expectancy on average by up to 13 months, with the highest decrease in city centres or areas with extensive domestic heating (Paper I). Our analysis indicated that particulate air pollution is an important public health issue as the estimated annual 462 premature deaths due to outdoor particles results in 6,034 YLL among the 650,225 residents. Moreover, the decrease in life expectancy can be more than a year because of local heating in neighbourhoods with dense small apartment buildings in Tartu, the second largest city in Estonia. When comparing our HIA results with other studies, our estimated average decrease of life expectancy of 0.63 years (7.6 months) is slightly lower than the assessment in Europe of 8.6 months (COMM, 2005). This indicates that major Estonian cities are nearly as polluted as European urban and rural areas on average.

We could also see that the societal costs of air pollution are relatively high. The estimates of the economic cost associated with premature mortality due to particulate pollution in Tallinn, Tartu, Kohtla-Järve, Narva, and Pärnu are on average €270 million annualy. This corresponds to an estimate of approximately 3 percent of the cities' GDP. Compared to economic effect assessments in other European regions, the estimations in Estonia are relatively high. For instance, in the EU assessment, it was estimated that the external costs of air pollution correspond to slightly more than 1 percent of the GDP of the EU (WHO, 2005b). The assessment from more polluted regions such as China give estimations as high as 3.3 percent of the GDP (The World Bank, 2007). In extreme cases, such as Beijing, there have been even higher estimated costs: 6.6 percent (Zhang et al., 2007). In Russia, it is as high as 6.5 percent of the GDP (Golub and Strukova, 2008).

Environmental health effects vary among different societal groups and special attention should be paid to vulnerable groups. Within any large population there is a wide range of vulnerability and certain individuals are at risk even at the lowest observed concentration levels (WHO, 2006). This includes people with underlying health conditions such as cardiovascular and lung diseases, asthmatics, socially deprived people, children, and the elderly. Up to now, some of the susceptible groups, like children, are not very well described in impact calculations. Nevertheless, recently it has been estimated that as many as 3.4 million premature births across 183 countries could be associated with fine particulate matter (Malley et al., 2017).

Our assessment in Tallinn showed that even though the average loss of all citizens' life expectancy is 0.63 years, the loss for premature mortality cases is greater, with an estimation of approximately 13 years. This indicates a much larger effect among at-risk groups. As life expectancy and healthy-lived years are lower in Estonia compared to EU15 countries, the vulnerable groups might be younger. However, the decrease in life expectancy among at-risk groups is similar to the Swedish results (Forsberg et al., 2005a; Gustafsson et al., 2018). When compared to Sweden, people in Estonia tend to die on average four years earlier, and detrimental effects appear in younger age groups.

Dispersion models have not been widely used in air pollution health effect studies. However, with modelled results we can attain a more detailed

picture of exposure gradients in different parts of cities. A station represents nearby neighbourhoods or areas with similar characteristics. During the study period, air pollution was monitored at three sites in Tallinn, one site in Kohtla-Järve and, for short periods, in Tartu, Narva and Pärnu. Furthermore, air pollution dispersion modelling can be used to construct scenarios of future trends and predict the extent of the health impact.

However, there are several limitations on this methodology. The main weakness of dispersion modelling is the poor quality of emissions data. To reduce the effect of this drawback, a database of local heating emissions was developed based on the results of a survey on fuel consumption (Kaasik et al., 2007). As the questionnaire was conducted several years ago in Tartu and those results were then adjusted to reflect the conditions in four other towns, certain differences in results may exist (e.g. prevailing sources of pollution). More frequent use of electric heaters as well as heat pumps and better insulation of houses might decrease the emissions from local heating. This can be one of the reasons for previous overestimations of emissions from local heating in Tartu and Pärnu, as has been shown in section 5.5, where the comparison with higher EF from RWC showed remarkable overestimation in comparison with measured values. The considerable difference (on average 22%) between all monitoring stations and modelled PM levels is an important factor in the reliability of the results. Thus, we should be careful in applying the results. But as the concentrations have been in some places overestimated and elsewhere underestimated, the uncertainty might not be so crucial.

Estimates of the emission factors for traffic pollution dispersion modelling were determined using CORINAIR (EAA, 2007). As there are negligible differences in car usage and climate, the differences are predictable. The modelled PM concentrations in Tallinn showed relative agreement with measured values in the residential areas and close to busy streets; however, there was a considerable underestimation in the industrial area (Orru et al., 2009b).

One of the crucial issues in HIA process is the selection of the E-R function, as it also has been discussed previously (Gustafsson et al., 2018; WHO, 2013). In our HIA, we used the relationships from the American Cancer Society (ACS) study. The sensitivity analysis in Paper I

was made using the E-R relationship from the same study but with a different baseline mortality indicator. A question arose about whether we can carry over the E-R function from the U.S. to the Estonian context. In general the applied E-R function is similar to later meta coefficients, where European studies have also been included (Hoek et al., 2013). Nevertheless, the pollution sources in Estonia are different, e.g. originating more from local heating. Additionally, the measuring sites might be dissimilar since primarily urban background levels are more regulated and monitored in the U.S. than in urban areas in Europe. Considering that the ACS study is the biggest air pollution cohort study including over 100 metropolitan areas, it should show average E-R function for all kinds of areas with multiple sources (Pope et al., 2002). Support for this statement can be found in the study by Jerret et al. (2005), an analysis of ACS participants from California, where traffic-induced particles explain a bigger proportion of gradients in PM pollution and where E-R coefficients were nearly three times higher. Moreover, extended analyses by Krewski et al. (2009) showed various E-R relationships in different parts of the country. In some later health impact assessments, different E-R functions have been applied for different source-specific fine particles (Gustafsson et al., 2018). In general, this gave a broader picture of the health effects than when only total fine particles effects were considered. Thus, when conducting health impact assessments, prevailing pollution sources should be considered in the future in Estonia as well.

6.2. The quality of emission data from household appliances

In general, there is lack of information concerning the characterisation of emissions from the residential sector in north-east Europe (Aurela et al., 2015; Elser et al., 2016; Vlachou et al., 2018). According to the Estonian Construction Registry there are around 164,000 households (30% of the total households) using wood for heating purposes, around 77% of which employ different kinds of masonry heaters and stoves while the rest mostly use local central heating boilers. In Estonia wood and wood chips account for > 90% of the fuel used for residential heating (Loosaar et al., 2008). According to an evaluation by members of the Estonian Chamber of Chimney Sweeps (Kupri, 2014), in addition to wood, paper and cardboard waste, people also tend to burn Tetra Paks, sanitary napkins, diapers, various plastic packages, shoes, textiles, etc. It is difficult to assess the exact number of people who still practice

burning MSW since such activities are done clandestinely (Kupri, 2015b). The ME-2 analysis of Q-ACSM and AMS datasets from Tartu showed that during the heating season, the plastic- or waste burning-related factor appeared (Elser et al., 2016; Maasikmets et al., 2015a; Vlachou et al., 2018) or its markers like terephtalic acid could be identified from samples measured in residential areas (Kupri et al., 2018). Presumable, some households burn MSW in their domestic fireplaces either to reduce fuel costs or to avoid disposal fees (Watson, 2012). In developed countries the fraction of waste burned residentially is often estimated based on the waste collection rate (IPCC, 2006; Wiedinmyer et al., 2014), which for Estonia was more than 95% in 2014 (Statistics Estonia, 2015). Nevertheless, this method does not take into account other relevant aspects, as the MSW burning rate in households is not only dependent on the development rate of the waste collection system in the country, but also depends on people's habitual behaviour (Kupri, 2015a) and is mostly driven by poor knowledge about the negative impacts of MSW burning. The available evidence indicates that waste burning in domestic conditions can be a significant generator of dioxins and, particularly, of PAHs. These emissions should therefore be reduced and eliminated wherever possible (Watson, 2012).

Within our experiments (Paper II), particulate number (PN), mass (PM) and HCl, CO_2 concentrations rose during the fuel-adding process and CH_4 level rose during the mixing of fuels (Paper II, Supporting Material, Figure S1). After adding fuel, CH_4 concentrations decreased, including a slight decrease in the chamber temperature. CH_4 emissions are a result of excessively low combustion temperatures, overly short residence times or lack of available O_2 (Van Loo and Koppejan, 2008). Similar results may occur in an 'average household' which is burning waste. During our experiments, MSW was added to the burning process in a similar way. In real life, the MSW content and adding process may vary from batch to batch. For a more homogenous fuel mix during the experiments shredded MSW could be used, but in our experiments this was avoided, as this does not represent the situation of how MSW is burned by 'average' people in households. It was also observed that during the firing phase and after adding fuel, the PM size distribution changed slightly to a bigger size fraction (Paper II, Supporting material, Figure S2). A similar tendency was also observed by Tissari et al. (2009), where they noticed that the size distributions were widest during the firing phase when the average size of particles was also larger. This was

probably caused by insufficient air supply, insufficient mixing of air and fuel and lower burning temperature.

It was found that during the wood and MSW mixture burning tests the mean $PM_{2.5}$ EF was 1,027.33 mg/MJ, which was around four times higher than the clean wood mean EF of $PM_{2.5}$ from the old-type masonry heater (Teinemaa et al., 2013) and around 43 times higher than the clean-wood mean EF of $PM_{2.5}$ obtained from the advanced masonry heater (Maasikmets et al., 2015b).

Chloride compounds have been found to be important precursors to PCDD/F formation under low temperature burning conditions (Kuzuhara et al., 2003). In our experiments, the chamber temperature increased rapidly up to 300°C at the beginning and approximately after 1 hour reached a maximum temperature of around 400°C, which shows that in this temperature range PCDD/F formation is favoured. Mean PCDD/F concentrations were in a range of 0.0116–0.1550 ng I-TEQ Nm^3 (11% O_2) during the experiments, and are generally in the same range of limit value (0.1 ng I-TEQ Nm^3, 11% O_2) set for the MSW incineration plants. Nevertheless, it should be taken into account that this limit value is set for the large waste incineration plants (such as Iru Power Plant in Estonia), where emissions are regularly controlled and monitored. Comparing the PCDD/F EF obtained from the MSW burning experiments (mean EF 0.059 ng I-TEQ MJ) with the clean wood burning tests measured previously by Teinemaa et al. (2013) and Maasikmets et al. (2015b), it can be seen that clean wood PCDD/F EF for the old-type heater was 0.013 ng I-TEQ MJ and for the newer heater type on average 0.009 ng I- TEQ MJ. Thus using MSW in a household heater may increase carcinogenic PCDD/F emissions at least 4.5 times on average. Our results show that household appliances can be important sources of toxic compounds if MSW is burned with wood.

Another important factor regarding the PCDD/F formation is the temperature inside of the heater hearth and the amount of available oxygen for the burning process, which during our experiments mostly favoured PCDD/F formation. As during the MSW burning tests we tried to simulate 'average' user habits and based on interviews with chimney sweeps, it was assumed that many users are trying to keep burning process as long as possible in order 'to get more energy out of it'. This leads to inefficient burning conditions, longer smouldering

period due to insufficient oxygen, and most probably also to lower temperatures inside the heaters. Besides the elevated particles and PCDD/F emissions, much higher PAH (incl. benzo[a]pyrene) and HCB EF levels in comparison with clean wood tests (Maasikmets et al., 2015b; Teinemaa et al., 2013) were observed. It is important to notice that in several countries, including Estonia, high benzo(a)pyrene ambient air concentrations have been estimated and measured (EEA, 2018a; Guerreiro et al., 2016).

The accuracy of EF has a central impact on the quality of emission inventories and actual emissions may be twice as high as during ideal operation, whereas improper handling can raise emissions even ten times or, in some cases, even more than hundred times (Nussbaumer et al., 2008), thus the user has large impact on real emissions (Fachinger et al., 2017). Within our study we tried to simulate burning according to how the 'average' user does it in their household, based on assumptions given by potters and chimney sweeps. Nevertheless, major uncertainties about the real-world and laboratory scale burning conditions may remain as each individual has their own strategy for how to operate the heater and stove.

Further, the emission sampling technique has a great impact on measured emission values. Various sampling techniques are used for the PM sampling from the emission gases. The most essential are filter measurements, measuring only solid particles (SP), and dilution tunnel (DT) measurements, measuring solid particles and condensable organics (or semi-volatile organics). It has been seen that a difference on the order of up to five times between the absolute PM emissions depending on the choice to use an SP- or DT-based EF may occur (Denier van der Gon et al., 2015). Seljeskog et al. (2017) has reported in average 6.5 times higher EF with DT-based technique in comparison with SP-method. The main difference between the two methods is that using the SP method mostly solid particles are measured and with the DT method condensable organics are also captured, which may lead to an underestimation of total mass concentrations by the SP method. Within the DT method, there is an attempt to include and simulate the process of particles exiting the chimney, where two important processes influence the fate of particles: cooling and dilution. Flue gases coming out of the chimney are never only cooled; the cooling and dilution occur together (Denier van der Gon et al., 2015). In general condensables are

important in poor combustion conditions, where the mass of them can exceed the mass of solid particles and thus evaluating the impact of wood combustion on the quality of ambient air should be considered (Nussbaumer et al., 2008).

European countries use both methods for EF calculations as both methods are standardized. In addition, the EMEP/EEA guidebook consists of EF measured either with the SP or DT method (EEA, 2016), whereas until now it is still not clearly stated which method was used for the EMEP/EEA EF calculation. Furthermore, national EF, used in official reporting, show considerable variation, even if they are obtained using the same type of measurement method (Denier van der Gon et al., 2015). Within our tests, emission samples from the hot-flue gas using Dekati® hot ejector diluter were taken using filtered air for the emission gas dilution and PM concentrations were measured using ELPI+ and, in addition, gravimetric sampling (the SP method) was used. In previous studies (Maasikmets et al., 2015b; Teinemaa et al., 2013), hot flue gas measurements were conducted using gravimetric sampling (the SP method). Theoretically the ELPI+ method also allows to do gravimetric sampling, but within our tests only online measured particle number concentrations from ELPI+ were used and gravimetric samples with the Dekati® 3-stage impactor were additionally taken. Normally during the biomass burning experiments, rather high PM concentrations occur, which means that for the online instrumentation around 100 times hot dilution are needed (in order not to oversaturate the instruments and avoid condensation) and this is not fully in line with dilution ratios used normally (DR~10) by the DT method. The hot dilution avoids condensation and hence enables to identify the particles in the same way that they were found in the stack (i.e., SP), but by gathering information on the particle size and number instead of the total particle mass (Nussbaumer et al., 2008). As within this thesis only EF results from the SP method were used, it may thus lead to an underestimation of measured results regarding the organic part and in the future comparison measurements between the SP and DT methods are needed. Nevertheless, it can be assumed based on the modelled and measured $PM_{2.5}$ concentrations within this thesis that the difference between the SP and DT methods cannot be five times higher as proposed in literature referred earlier, as already within this study it can be seen that average RWC $PM_{2.5}$ EF (125.05 mg/MJ) caused some overestimation in comparison with measured values. For instance

in Germany for RWC sector EF 105 mg/MJ is used (Struschka et al., 2008), which is similar to our result.

Based on previous measurements from burning wood logs (Maasikmets et al., 2015b; Teinemaa et al., 2013) and wood logs + MSW (Paper II) in laboratory conditions, weighted average $PM_{2.5}$ EF was calculated (Figure 5). Regarding waste burning, two scenarios were evaluated - 2% MSW and 45% MSW scenarios - whereas the percentage shows the share of the population that burns MSW in their homes. The two scenarios are based on assumptions used in Estonian official air pollutants and GHG emission inventories. In the GHG emission inventory it is assumed that at maximum 2% of the population burns MSW in their homes regularly (NIR, 2018) and in the air pollutants emission inventory it is assumed that 45% of the population may burn some MSW in their households (EEEA, 2018a). Both assumptions are based on expert opinions and may carry large uncertainties; thus further clarifications regarding this topic are needed. Within this thesis it was shown that in most cases 45% MSW scenario gave remarkable higher results (Figure 11 and Figure 15) in comparison with measured $PM_{2.5}$ ambient concentrations. The 2% MSW scenario had a mostly good correlation with measured values, although this scenario also overestimated yearly average concentration by around 12% and during the 2016/17 heating season by around 6%, in comparison with the measured values (Figure 17 and Figure 15). Based on measurements conducted with a Q-ACSM and aethalometer, which allows to separate the biomass burning part from the measured particle concentration, it was seen that, although the correlation between the modelled 2% MSW scenario and measured concentrations is good, modelled results are somewhat higher for the biomass part, which indicates that for RWC $PM_{2.5}$ EF may be even lower, as calculated (125.05 mg/MJ) within this thesis (Figure 5). In addition, assumptions made when calculating the weighted RWC $PM_{2.5}$ EF may need to be revised. As the BBOA and eBC_{bb} shares were comparable with previous studies (Elser et al., 2016) and with measurements from similar locations (Aurela et al., 2015; Helin et al., 2018), it can be assumed that normally the RWC share from the total $PM_{2.5}$ cannot be much higher than what was measured within this study (~2 $\mu g/m^3$ as a yearly average). In addition, there might be uncertainties in other modelled sectors (traffic exhaust, industry and regional background), which were not validated thoroughly within this study, but should be done in the future. Moreover, there might be uncertainties related to the measurement instrumentation.

For example, it has been shown previously that eBC measurements are very sensitive to the Ångström exponent (Drinovec et al., 2015; Helin et al., 2018; Sandradewi et al., 2008; Zotter et al., 2016). Furthermore, knowledge about the Q-ACSM proper calibration, including international comparison campaigns (Crenn et al., 2015; Fröhlich et al., 2015) and data analysis, are improving worldwide (Canonaco et al., 2013; Canonaco et al., 2015). Thus, uncertainties regarding Q-ACSM measurements and data analysis are expected to decrease.

Further developments regarding RWC source location and more precise source-specific emission estimations are needed. Within this study we have compiled RWC EDB combining data from the construction and cadastral registry, which gives us information about the source location (with cadastral precision) and data about the used heating system and living space in m^2. For now, all the RWC sources are treated as point sources and for the chimney location cadastral central coordinates are used. In reality the situation may vary, as the exact location of the house chimney in cadastral unit is in most cases not exactly in the centre of the cadastral unit. On the other hand, this information is not so crucial if modelling is done on a larger urban scale. As there is no data about the chimney heights (m) and flue gas velocity (m/s) in construction registry database, it was assumed that all RWC sources are 10 m in height and flue gas velocity was assumed to be 2 m/s. Those numbers are based on rough estimations based on previous measurements (Teinemaa et al., 2013) and surely they can vary among households. Regarding the modelling purpose, the chimney height and flue gas velocity mostly influence the emission dilution conditions at the local level, but taken into account all other uncertainties related to emissions and their dynamics, it is assumed that those aspects are not most relevant regarding the upgrade of EDB in the nearest future.

The most crucial aspects requiring further research on EF are the data about the heating systems used in households and data about the house insulation, as these directly affect fuel consumption, thus having a direct effect on air emissions. In the future the construction registry database should be upgraded with the population and household census data. Another option could be to combine the chimney sweeps' database with the construction registry, but for the time being this database is under development by the Estonian Rescue Board. Previously, Kaasik et al. (2007) conducted a survey on fuel consumption in households, which

could be updated in several cities to help improve the quality of RWC EDB.

In addition, there is a need to upgrade RWC EDB regarding emission dynamics. So far eBC data from an aethalometer has been used, which generally gives good results, but due to its static assumptions, it could be improved by using some additional dynamic parameter in order to identify more precisely at which time emissions from the chimney are released. One option would be to use the chimney temperature data, in order to assess the beginning and end of the heating process. For this purpose, a pilot study with five temperature sensors in Tartu area started last year, in order to see whether sensors inside the chimney are possible to use in longer term for the emission dynamic estimation. Further analysis about the first results, will follow in the nearest future (Keernik et al., in preparation).

6.3. Uncertainties in non-exhaust-related emissions

For the non-exhaust emissions, uncertainties in the emission inventories are substantial, because there is considerable uncertainty about the type of activity as well as the related EF (Denier van der Gon et al., 2018). Up until the early 1990s, road transport emissions were dominated (80–90%) by exhaust emissions (Denier van der Gon et al., 2013), but nowadays about half of traffic PM_{10} emissions derive from non-exhaust processes (Amato, 2018). This indicates that traffic exhaust emissions regulations were mostly successful, but negligible attention has been paid to the reduction of non-exhaust emissions. According to the Estonian air emission inventory, non-exhaust PM_{10} emissions were 49.6% of the total traffic-related PM_{10} emissions in 2014 (EEEA, 2018b), which is comparable to other EU countries (Denier van der Gon et al., 2018). While the contribution from non-exhaust emissions is equal or even higher than exhaust PM_{10} emissions in most EU countries, this is not the case for $PM_{2.5}$. For example, in Estonia the share of non-exhaust $PM_{2.5}$ from the total traffic related $PM_{2.5}$ emissions is about 35% (EEEA, 2018b). According to EEA (2016), about 50% of the wear PM_{10} emissions are assumed to be $PM_{2.5}$, whereas for exhaust emissions it is almost 100%. Therefore, exhaust still dominates in $PM_{2.5}$ emissions and will continue to dominate for a number of years (Denier van der Gon et al., 2018). On the other hand, data about the non-exhaust PM size distribution is scarce and often contradictory (Padoan and Amato,

2018). Thus the exact share of different PM sizes remains highly uncertain and at least during our tests such a high share of $PM_{2.5}$ in PM_{10} was not observed (Paper III). This may be caused by the fact that background concentrations were always measured simultaneously and later subtracted from the results. Similar to our results, Kupiainen et al. (2005) also found a particle mass-size distribution with a maximum well above 2.5 μm, both with friction tyres and studded tyres.

Based on measured non-exhaust EF, historical total non-exhaust PM emissions were calculated for Estonia and a national emission inventory update was proposed based on it (Paju et al., 2014). It can be seen from Figure 20 that PM_{10} emissions from the paved road in 2010 were around 224 Tonnes and around 150 Tonnes were emitted due to usage of studded tyres. Comparing results with the officially reported non-exhaust PM_{10} total emissions, it shows that officially reported non-exhaust emissions are somewhat higher (254 vs 224 t/a in 2010), but in general results are comparable (Figure 20).

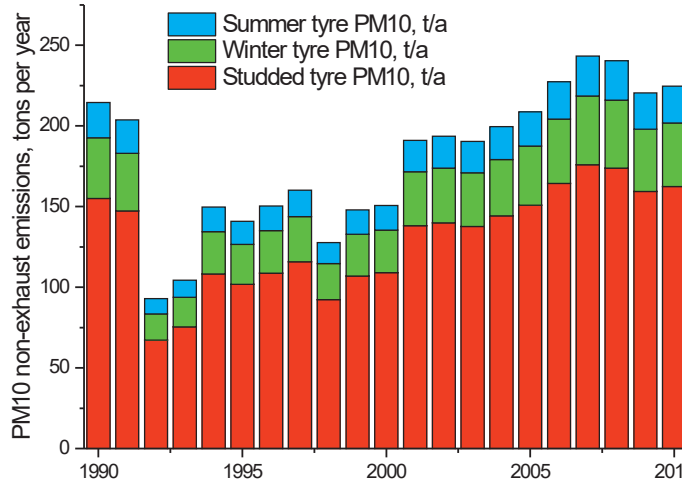

Figure 20. Non-exhaust PM_{10} emissions from the paved roads (Paju et al., 2014)

Comparing officially reported 2014 total non-exhaust PM_{10} emissions with the total non-exhaust PM_{10} emissions based on measured PM_{10} EF (Paper III) (Figure 21), the officially reported total emissions are somewhat higher, but in general comparable. It should be noted that both methods use the same input data regarding the car fleet share and driven mileage, but the official inventory does not count the share of the studded tyres and does not include the days when studded tyres were

allowed during the year, assuming that same tyres are used throughout the whole year. In the end this might average out the differences in used EF and gives approximately the same total emission for both approaches. On the other hand, measured EF calculations were based on passenger car EF, which was used for all car types, whereas official emission inventories distinguish between EF for passenger cars, light heavy vehicles (LHV) and heavy duty vehicles (HDV). Bukowiecki et al. (2010) report LHV PM_{10} EF in a range of 24–50 mg/vkm and for HDV up to 498 mg/vkm. HDV contribution is estimated to be 5 to 10 times larger than the LDV EF (Denby et al., 2018). For the time being, no LHV or HDV EF were measured with the REAL system, but for the further emission inventory improvement, it would be necessary to carry out in the future measurements for other car types in Estonia, as literature results indicate large differences between passenger cars' LHV and HDV EF. Thus it may increase the total non-exhaust emissions.

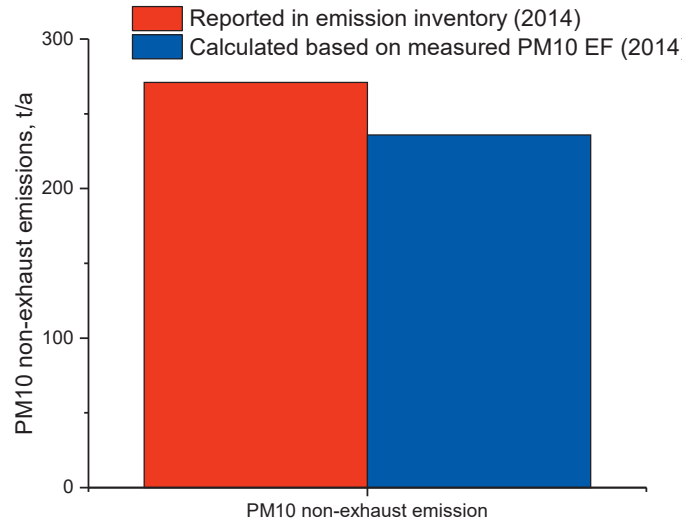

Figure 21. Comparison of total PM_{10} emissions from the non-exhaust sources in 2014, official EI submission vs measured EF-based calculation

Another important factor in non-exhaust PM_{10} emissions is the share of the non-paved roads in a country and emissions connected to roads. Gillies et al. (2005) investigated the influence of vehicle characteristics on the resuspension of road dust on unpaved roads and found that emissions had a strong linear relationship (in addition to vehicle speed) with vehicle weight and proposed a linear relationship among emission factor, velocity, and mass, based on their measurements on unpaved

roads with vehicles weighing between 1,200 kg and 18,000 kg. Mathissen et al. (2012) conducted PM_{10} emission measurements on unpaved roads in Germany and found that average PM_{10} EF for unpaved roads was 24,000 mg/vkm, so around 1,000 times higher than the paved road average EF. As there were around 15,000 km of paved and 24,500 km of unpaved roads in Estonia in 2010 (Paju et al., 2014), it is important to count emissions from unpaved roads. So far emissions from unpaved roads are not included in the Estonian air pollutants emission inventory, mainly to avoid possible double counting of non-exhaust emissions and possibly their very local influence, as most of the coarse mode PM from the unpaved roads is thought to deposit on nearby road surfaces and can be reemitted several times.

Adding emissions from the unpaved roads (PM_{10} EF = 19,760 mg/vkm measured in Estonia, Paju et al. (2014)), the PM_{10} emissions from the non-exhaust sector increase dramatically – around 80 times for the year 2010 (18,077 t/a from unpaved vs 224 t/a from the paved roads), thus making this sector an important contributor to the coarse mode PM. Further investigations regarding the unpaved road emissions should be conducted in order to evaluate their possible effect on the local and regional air quality.

The somewhat higher EF of non-studded tyres, when compared to summer tyres, is caused by their softer material and deeper treads that create a stronger vacuum when contacting pavement, resulting in a greater number of fine particles emitted into the air (Paper III). Summer tyre material is harder and road surfaces are generally cleaner in the summer.

The greater emission of particles at higher speeds is caused by the stronger forces acting between the tyre and the road surface; these produce more wear on both the pavement and the tyre. Higher speed also causes more air turbulence under the vehicle which lifts more particles off the road surface (Paper III).

The largest mass concentration of particles is produced in the coarser particle size range, varying somewhat depending on the tyre type. Studded tyres produce a somewhat greater proportion of coarser particles when compared to non-studded and summer tyres, while the particle size with the highest mass concentration is around 8 μm for both non-studded

and studded tyres (Paper III, Figure 5). The more varied size fraction distribution among studded tyres, when compared to non-studded and summer tyres, might be explained by differences between studs.

In Paper III it was found that preliminary testing confirmed the suitability of REAL for the measurement of PM emission originating from vehicle tyres, brake pads and road pavement abrasion. REAL has the advantages of compatibility with different vehicles and of an autonomous electrical power that allows the use of different measurement devices. While measuring PM originating from pavement and vehicle wearing parts, the system can also measure the composition of vehicle exhaust gases under actual driving conditions. Thus, PM emissions of the vehicle can be measured under actual driving conditions. Also, REAL can measure PM resuspension behind both wheels simultaneously. This opens a future opportunity to study whether PM emission numbers depend on the sampling point location (middle or edge of the road) and to simultaneously study different tyre types. REAL adds the capability of real-time measurement of tyre and pavement temperature. This gives an opportunity to evaluate the effect of temperature on PM formation. Until now the relationship between temperature and PM formation has only been studied in laboratory conditions (Dahl et al., 2006). The present test with summer tyres showed that vehicle speed affects tyre temperature (Paper III, Figure 6), but there was no correlation between any measured particulate fraction and tyre temperature. There was a moderate polynomial correlation between vehicle speed and tyre temperature ($R^2 = 0.51$). Heat is generated in tyres mainly from the friction between molecules of continuous compression-tension or torsion (Oh et al., 1995). If the heat generation occurs faster than it can be transferred into the ambient air, it gradually increases the tyre temperature and reaches its maximum at the outermost ply or belt (Netscher et al., 2008). Increased temperature leads to increased emission of loosely bound reinforcing filler material and evaporation of semi-volatile softening oils (Dahl et al., 2006). Additionally Dahl et al. (2006) argue that the properties of the used oil mixture in tyres may determine whether or not homogeneous nucleation of gaseous precursors can produce significant quantities of nanometre-sized particles. In our test we could not observe any relationship between nanometre-size particles and vehicle speed. Probably the tyre temperature did not reach the necessary temperature where the loosely bound material will start to evaporate. It may be that the age of the tyre also plays an important

role in this case (Paper III). Further research is needed to investigate the nanometre-size particle formation from the tyre material.

There are plans to equip REAL with sensors for measuring continuously the pavement humidity, as humidity can affect formation and uplift of fine particulates (Bukowiecki et al., 2010). A humidity sensor (e.g., MARWIS [Lufft, GmbH]) could be added for the future measurements in order to identify pavement humidity in real-time mode without contacting the pavement surface.

The comparability of the measurement results is also complicated by the lack of uniform standards for measured PM size distribution and measurement methods. Many similar measurements have been performed with optical analysers with an approximately 300 nm lower end of PM size resolution, while for instance ELPI+ and SMPS analysers can measure considerably smaller size fractions of fine particulates. Moreover, with ELPI+ the proportion of PM originating from worn rubber in the samples can be assessed by later analysis of filters and may be used for the non-exhaust particle chemical composition analyses (Paper III).

Within the thesis the modelled non-exhaust concentrations had a poor correlation with the measured ambient air $PM_{2.5–10}$ data. The dynamics, in particular, did not follow the same pattern as real ambient concentrations. The main reason for this could be that we were unable to assess salting and sanding episodes in Tartu and the actual wetness of the road surface is not well defined in the model calculations. The measured annual average $PM_{2.5–10}$ concentration in Station 1 was 9.06 $\mu g/m^3$, and the modelled results for EF 64 mg/vkm and EF 460 mg/vkm were 3.63 and 7.56 $\mu g/m^3$ respectively, indicating that somewhat higher non-exhaust emissions are expected to occur in reality. Another important factor might be, that within this thesis for all car types the same EF (64 or 460 mg/vkm) was applied, which seems to cause not-comparable results with the measured $PM_{2.5–10}$ values.

6.4. Livestock farming emissions

There was a clear seasonal variation in measured indoor PM and NH_3 concentrations between the warmer and colder periods. During the warmer period (from May to September) the concentration of the

different PM fractions, CO_2 and relative humidity inside the uninsulated loose housing cattle buildings was lower than in the colder period (Paper IV). Similar results for higher PM concentrations in the winter period were also reported by Purdy et al. (2009).

The uninsulated loose housing large-scale farms have shown lower inhalable and respirable airborne particle concentrations compared with insulated farms with tied housing, for example 380 $\mu g/m^3$ vs 70 $\mu g/m^3$ (Takai et al., 1998; Wathes et al., 1998). This might be associated with the amount of litter used on the farms. In contrast to cattle buildings, where cows are kept tethered, there are substantial volumes of bedding material used and renewed on a daily basis. Loose housing on large-scale dairy farms operate with minimal litter, or without any bedding at all. Also, in large-scale uninsulated loose housing farms, the distribution of litter is carried out according to need, usually once per week (Paper IV).

The NH_3 concentration in the air inside the cowsheds was most strongly correlated with the concentrations of the fine fractions of PM (Paper IV). A similar tendency has been observed by others (Reynolds et al., 1998; Takai et al., 2002). We did not find any significant relationships between the total concentration of PM and either the indoor temperature or the relative humidity in the cowsheds. However, when the temperature and RH increased, the concentration of total PM concentration decreased; there was weak negative correlation between these parameters. A rise in indoor temperature significantly reduced the concentrations of $PM_{1.0}$; $PM_{2.5}$ and PM_{10} (there was a strong negative correlation). The temperature and NH_3 concentrations inside the cattle buildings were positively correlated. As the NH_3 is a result of microbial processes, then a higher-than-optimal temperature would stimulate NH_3 production (Paper IV).

The correlation between the particulate matter concentrations and the relative humidity inside the cattle buildings is of interest. While the total PM concentration was weakly negatively correlated with relative humidity, the PM_{10}, and especially the $PM_{2.5}$ and $PM_{1.0}$, were strongly positively correlated with the relative humidity. The finest fractions of PM contain a large proportion of liquid components (water vapour and compounds incorporated with water). The higher moisture inside the cowshed was accompanied by a higher concentration of CO_2 (Paper IV).

The concentrations of particulate matter and fine particles inside the loose housing cowsheds depend a great deal on the particulate matter concentration of the outdoor air. In the analysis, the correlation between ambient and indoor air was different for PM_{10} and $PM_{2.5}$. The correlation between the inside and outside concentrations was better for fine particles, r = 0.208 (PM_{10}) and r = 0.365 ($PM_{2.5}$), respectively. The finer the particles, the more they are carried into the cowshed from outside while heavier coarser particles precipitate more rapidly. The fluctuation of the PM concentration inside the cowshed was primarily a result of animal activity and management routines (Paper IV).

Elevated NH_4^+ levels from the analysis of PM filters during winter were observed. The formation of particulate ammonium nitrate is not favoured thermodynamically during warmer periods. During the winter period, the ionic composition is the highest in the size range of 1 μm, while during the summer, the highest peak was around 0.5 μm. This indicates that during the winter period, particles inside the cowshed are probably more aged, which is caused by the regional pollution or due to the lower ventilation rate, which causes the formation of larger particles due to the longer stagnation of air inside the cowshed (Paper V).

In Paper V NH_3 background value assumed to be 1.92 $\mu g/m^3$, measured during 1 month in rural background near Tartu using Radiello® passive sampler (Maasikmets, 2007). For time being there is evidence that this background value might have been overestimated as online instrumentation (Picarro G2401, WS-CRDS) in Lahemaa background station is showing yearly average values in the range of 0.2 $\mu g/m^3$ and Kiss (2017) has estimated that IVL-type passive samplers may overestimate NH_3 concentrations. On the other hand there was no information available for time-being about comparison measurements with Radiello® and IVL-type passive samplers and with more precise online instrumentation like Picarro WS-CRDS.

In Paper V the average ventilation rate was 260.6 ± 12.1 m^3/h per LU and the highest ventilation rate occurred during the spring time. Ruus (2013) found that the ventilation rate in uninsulated cowsheds ranges from 110 m^3/h per LU to 392 m^3/h per LU during winter and summer time, respectively. According to the survey of Seedorf et al. (1998), across Northern Europe, the mean ventilation rate was 341 m^3/h for cattle farms, which is comparable with our result.

6.5. Effects of updated EF on air quality modelling

In the current thesis I applied the air quality modelling approach using Airviro Eulerian Advection-Diffusion grid dispersion model with two RWC scenarios: (1) for 2014 and the 2016–2017 heating season (December to May) and (2) for the whole of 2017. In most cases the 45% MSW scenario largely overestimates $PM_{2.5}$ concentrations in comparison with measured $PM_{2.5}$ values, whereas the 2% MSW scenario was generally in accord with measured and modelled values and had a mostly good correlation with measured values (Figure 11, Figure 15, Table 1). In Stations 2 and 4, the measured values were higher in comparison with the 2% MSW scenario modelled results (Figure 11), which was mostly caused by the local circumstances of the monitoring points. Stations 2 and 4 were located at gasoline stations and close to busy streets. In both gasoline stations near monitoring stations there were parking lots for cars and it was noticed several times during the campaigns that during the cold period people often leave their car running in the parking lot during their visit to the gasoline station shop or fast food restaurant. Thus, those additional emissions are not taken into account in modelling EDB-s. In addition, traffic exhaust EDB may need to be updated with newer traffic input data.

Used Airviro Eulerian Advection-Diffusion grid dispersion model has been previously compared with Airviro Gaussian and Lagrangean (Austal2000) model in Tartu area by Taidre (2017) using three year meteorological data and same RWC EDB as within this thesis. It was shown that Eulerian and Gaussian model gave in general comparable results, whereas in very stable conditions Eulerian model gave somewhat higher results in comparison with the Gaussian model, although it is also observed that Eulerian model gives somewhat better agreement with the measured values in Tartu area (Maasikmets et al., 2016).

On average organic material made up 61.5% of the total mass measured with the Q-ACSM, followed by sulphate (17.5%), nitrate (13.4%), ammonium (6.2%) and chloride (1.5%), which is in line with previous measurements (Elser et al., 2016). Average OA concentration was 2.18 $\mu g/m^3$, which is similar to modelled results by Denier van der Gon et al. (2015) and Ciarelli et al. (2017). The NR-$PM_{1.0}$ comprised on average 49.75% of the total $PM_{2.5}$ concentration, which is consistent with other findings (Aurela et al., 2015; Sun et al., 2012). The average contribution

of eBC to $PM_{2.5}$ was 21.52%, which is around two times higher compared to results measured in Helsinki residential areas (Aurela et al., 2015) and eBC_{bb} contribution to $PM_{2.5}$ was 14.87%, which shows that biomass burning is an important source of eBC in the Tartu area and is in line with previous findings by Elser et al. (2016). By summing NR-$PM_{1.0}$ and eBC, their contribution to total $PM_{2.5}$ mass concentration increases on average up to 71.27%. Between the NR-$PM_{1.0}$ and $PM_{2.5}$ concentrations, a high Pearson correlation ($r = 0.745$) was observed and if adding eBC to NR-$PM_{1.0}$, an even higher correlation ($r = 0.817$) was found, which is consistent with other findings (Aurela et al., 2015; Budisulistiorini et al., 2014; Elser et al., 2016).

BBOA had rather stable contribution during the whole 2016–2017 heating season period, ranging from 24.6% to 26.1% of the total OA as shown previously in Figure 14. This is similar to Elser et al. (2016) and had its prominent m/z peaks at 60 and 73, which are identified as fragments from anhydrous sugars present in biomass smoke (Alfarra et al., 2007). If adding eBC_{bb} to BBOA, the average concentration increases to 2.05 $\mu g/m^3$, which is on average 22% of the total $PM_{2.5}$ concentration. Good correlation ($r = 0.739$) between BBOA and eBC_{bb} was found, which is somewhat higher compared to the results found by Elser et al. (2016). The ratio of BBOA and eBC_{bb} was on average 0.48, indicating that on average eBC_{bb} concentrations are higher compared to BBOA. In nearby Helsinki (Aurela et al., 2015) the BBOA/eBC_{bb} ratio was 0.8, but Crippa et al. (2013) and Elser et al. (2016) have reported much higher ratios ranging from 4 to 15. In the current thesis correlations between chloride and BBOA ($r = 0.897$) and between chloride and eBC_{bb} ($r = 0.498$) were found. This is in line with findings by Aurela et al. (2015), where correlation between BBOA and chloride was 0.760. 'Fresh smoke' may contain potassium chloride (KCl) which may largely be present during the flaming period (Li et al., 2003; Liu et al., 2000), whereas 'aged smoke' contains more potassium nitrate (KNO_3) and potassium sulphate (K_2SO_4) (Li et al., 2003). On the other hand, there is also evidence that ambient air chlorides are related to possible garbage burning (Li et al., 2012). In addition Bloss et al. (submitted) has noticed during the wood + MSW emission measurements elevated chloride concentrations during the MSW adding to the burning process. As Kupri et al. (2018) found good correlation between eBC_{bb}, BBOA and plastic burning related markers like terephtalic acid, it can be assumed that some part of chloride may be influenced by local waste burning.

In the current thesis it was found that HOA (5.1% of the total OA concentration) is mostly associated with sources such as traffic and has a clear minimum during the night and peaks during the morning, and evening rush hours. HOA contribution to OA in Tartu was somewhat lower compared to results found elsewhere in Europe, where the average contribution in range of 11% ± 6% of OA has been found (Crippa et al., 2014). In Helsinki average HOA contribution as high as 33% have been measured (Aurela et al., 2015). Adding eBC_{ff} to HOA will increase the mean traffic-related concentration from 0.14 to 0.76 $\mu g/m^3$ (8.2% of the total $PM_{2.5}$). HOA correlates well with eBC_{ff} ($r = 0.591$) and NO_x ($r = 0.794$). The HOA and eBC_{ff} ratio was 0.23, which is comparable to other results (Chirico et al., 2010; Crippa et al., 2013; Favez et al., 2010). The lower HOA contribution in Tartu might be influenced by the seasonal contribution of sources and local circumstances as the monitoring station is surrounded by residential houses and busy streets are somewhat distant from monitoring station (100 m away).

COA (5.7%–7.1% of OA mass) is mostly characterized by a prominent diurnal pattern with increases during meal times and having higher contribution from oxygenated ions at m/z 55 and m/z 57 (Mohr et al., 2012). COA contribution in Tartu is much smaller compared to studies conducted in Paris (18% of the OA mass; Crippa et al. (2013)), in London (20% of the OA mass; Ots et al. (2016), in Barcelona (15% of the OA mass; Crippa et al. (2014) and in previous campaign in Tartu (20%–26% of the OA mass; Elser et al. (2016). However, in the previous Tartu campaign no clear COA factor was present due to mixing with other sources from the residential sector (Elser et al., 2016). Similarly Aurela et al. (2015) did not find a COA factor in Helsinki. As the cooking contribution is not easily resolved even for urban sites due to the similarity of its mass spectrum with the one of HOA in unit mass resolution (Crippa et al., 2014), it might be that some part of COA is included in HOA factor and opposite. To clarify the HOA and COA contributions during the whole year cycle, further analysis is needed, which will be performed during the long-term Q-ACSM dataset analysis by Keernik et al. (in preparation).

As BBOA, HOA and COA are counted as primary OA, it is additionally possible to separate from the total OA the secondary OA part, which is important in order to distinguish between local and regional sources and evaluate their possible effect on measured concentrations. Two

secondary OA sources were separated - the LV-OOA and SV-OOA -both having high signals of m/z 44 (CO^+_2). LV-OOA was identified as a second major OA fraction, contributing from 27.1% to 34.8% to the total OA mass, having a somewhat lower m/z 43 peak compared to SV-OOA. Good correlation between LV-OOA and sulphate was found (r = 0.774). SV-OOA contributes to the total OA mass in range from 29% to 33.1% and had good correlation with ammonium nitrate (r = 0.587).

Comparing the RWC share from the 2% MSW scenario and from the BBOA + eBC_{bb} data (2016–2017 heating season), it could be seen that air pollution dispersion modelling slightly overestimates the daily mean concentrations (Figure 22). A moderate correlation between measured and modelled values was observed (r = 0.424). In the diurnal cycle, the RWC 2% MSW scenario seems to overestimate the evening peak by a factor of two (Figure 23), although the morning (between 8 and 9 a.m.) and evening (between 7 and 8 p.m.) peaks are occurring in the same time for the modelled and measured results.

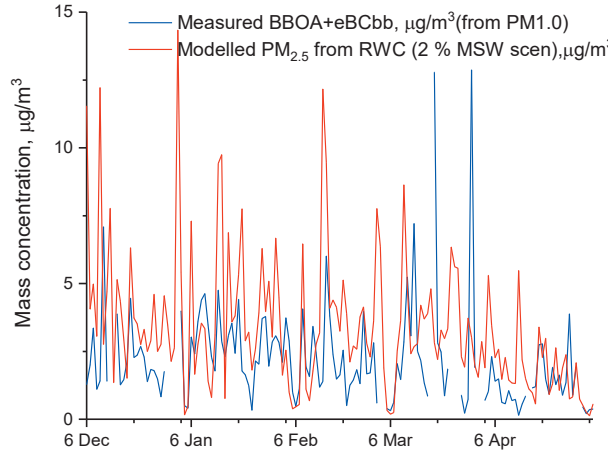

Figure 22. Daily mean BBOA+BC_{bb} measured and modelled $PM_{2.5}$ (RWC 2% scenario) concentrations (2016–2017 heating season)

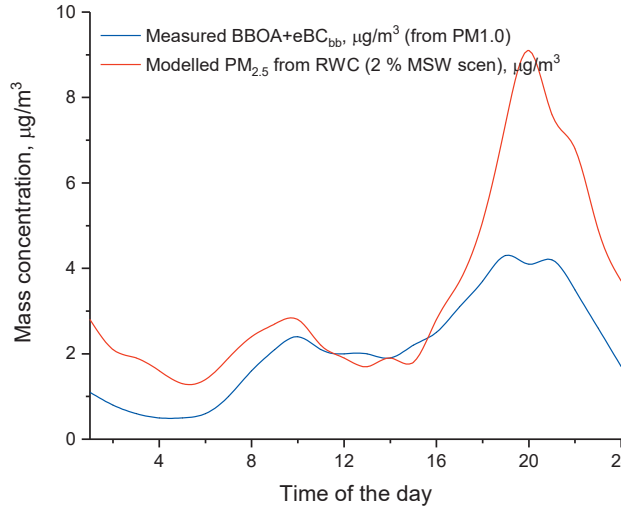

Figure 23. Diurnal cycle of modelled $PM_{2.5}$ (RWC 2% MSW scenario) and measured $BBOA+eBC_{bb}$ concentrations (2016–2017 heating season)

Modelled $PM_{2.5}$ results from the RWC sector using 2% MSW scenario and measured eBC_{bb} (Figure 24) had a good correlation ($r = 0.794$) during the yearly cycle. The diurnal cycle during the whole year (Figure 25) shows that modelled results ($PM_{2.5}$ from RWC) are higher (around three times) during the evening peak compared to measured eBC_{bb} results. Comparing modelled $PM_{2.5}$ concentrations (including the RWC 2% MSW scenario, traffic exhaust, industry, livestock farming and $PM_{2.5}$ background concentrations) with the mean diurnal cycle (Figure 26), the measured $PM_{2.5}$ cycle is much 'flatter' and does not have such clear prominent morning and evening peaks as the modelled result. Also, in this case, the modelled evening peak is somewhat (ca. 1.5 times) higher than the measured $PM_{2.5}$ values, although the difference is smaller when compared to the results from the 2016–2017 heating season.

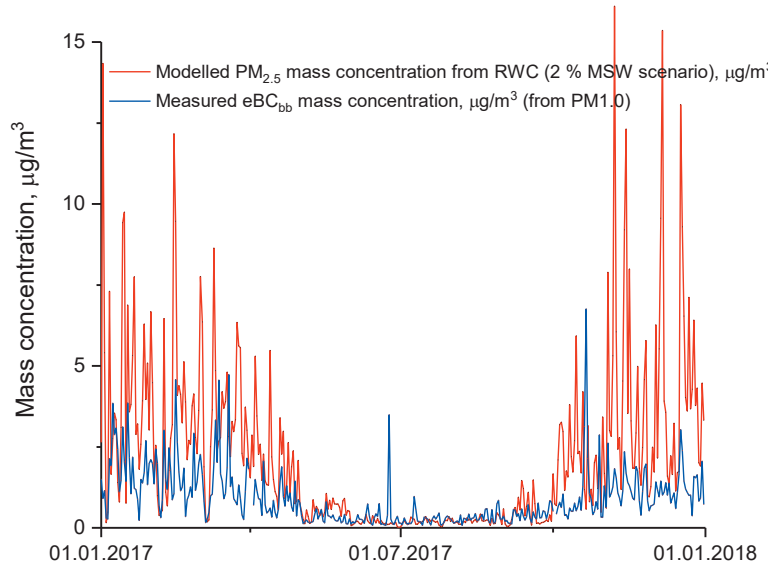

Figure 24. Modelled $PM_{2.5}$ from RWC (2%MSW scenario) and measured eBC_{bb}, μg/m^3 (2017)

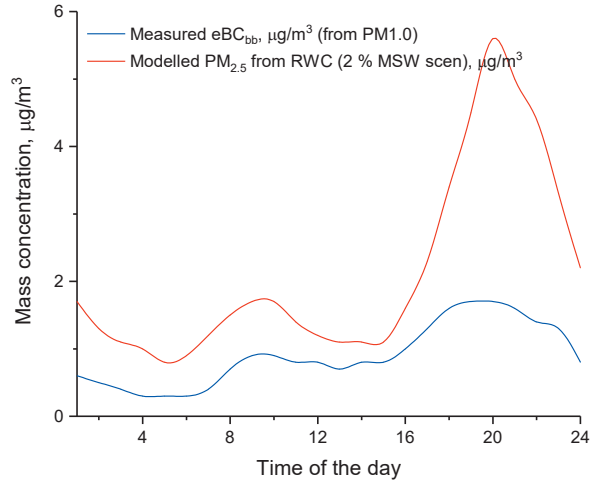

Figure 25. Diurnal cycle of modelled $PM_{2.5}$ (RWC 2% MSW scenario) and measured eBC_{bb} concentrations μg/m^3 (2017)

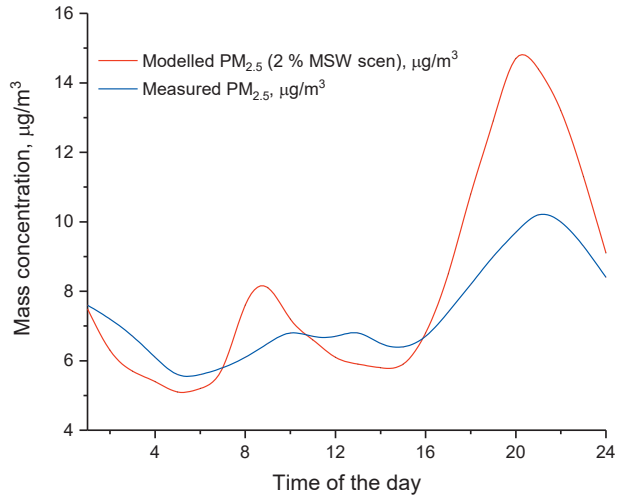

Figure 26. Diurnal cycle of modelled $PM_{2.5}$ (2% MSW scenario, includes RWC, traffic exhaust, industry, livestock farming and background) and measured $PM_{2.5}$ concentrations μg/m^3 (2017)

From the 2017 dataset it could be seen that eBC_{bb} and eBC_{ff} are contributing on average 0.90 ± 1.64 and 0.72 ± 0.94 μg/m^3, respectively, to $PM_{2.5}$ concentrations (Figure 17). This is somewhat higher than the results from Helin et al. (2018), where they have measured eBC in Helsinki suburban areas near detached houses and have yearly average (Dec. 2015–Dec. 2016) concentrations of 0.39 ± 0.80 and 0.49 ± 0.77 μg/m^3 for eBC_{bb} and eBC_{ff}, respectively. On the other hand, Helin et al. (2018) has measured comparable yearly average $PM_{2.5}$ concentrations in the Helsinki suburban area (7.3 ± 6.9 μg/m^3) as measured in Tartu at Station 1 (7.3 ± 7.7 μg/m^3) in 2017. A moderate negative correlation ($r = -0.484$) was observed between air temperature and measured biomass burning-related eBC (eBC_{bb}) concentration in Station 1, which is similar to the Helsinki results (Helin et al., 2018), whereas no correlation ($r = 0.034$) between traffic-related eBC (eBC_{ff}) and air temperature was found. The negative correlation between air temperature and eBC_{bb} indicates that RWC related emissions increase when the temperature decreases. Thus more heating and more emissions occur during colder periods.

Regarding the possible MSW burning in households, it is difficult to distinguish between aerosols which are emitted from pure wood or from the MSW-containing burning process, as using ME-2 analysis normally predefined mass spectra are used and no wood + MSW containing AMS

or ACSM mass spectra can be found in publicly available datasets yet (Ulbrich et al., 2009). Using the dataset of Mohr et al. (2009) on plastic burning and HOA, it could be seen that both mass spectra are quite similar (Figure 27). During both processes fresh hydrocarbons are emitted and it can be assumed that if using PMF or ME-2 analysis, waste burning aerosols might be 'hidden' within some other factor, most probably in BBOA and HOA factor. During certain plastic combustion experiments Mohr et al. (2009) found prominent peaks at m/z 55 and m/z 57 which was also seen by Bloss et al. (submitted), who did laboratory scale burning experiments using wood + MSW in masonry heater. In addition Bloss et al. (submitted) found prominent peaks at m/z 60, 69, 71, 77 and 83 and increased concentrations of inorganic salts (incl. HCl) and metals were found during the MSW adding process. Further research is needed in order to develop methods for waste burning aerosol quantification.

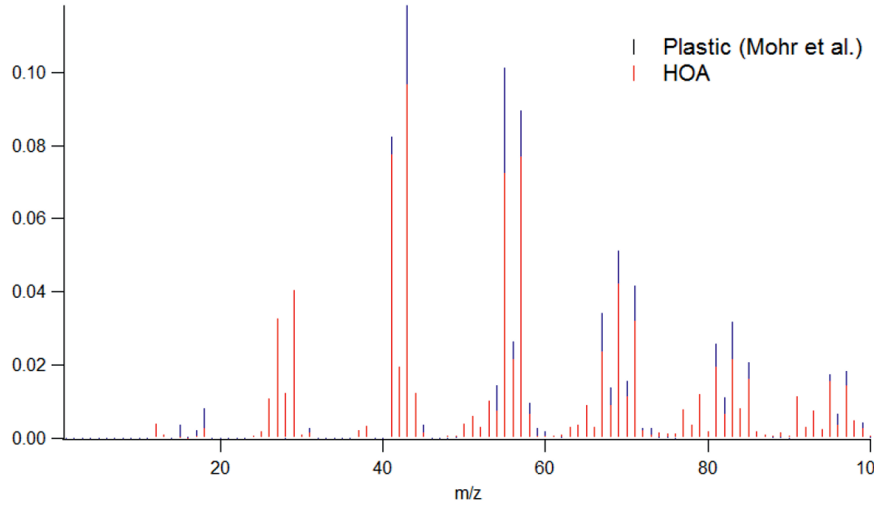

Figure 27. Mass spectra from plastic burning and HOA

Improved EDBs were also used to compare the earlier modelled results from Paper I (Figure 28). It could be seen that new modelling gave improved results regarding more precisely located hotspots compared to previous modelling results (Figure 29). In addition, the modelled results were also improved when compared with measured $PM_{2.5}$ in Station 1. The previous model (Paper I) overestimated by around 22% the measured $PM_{2.5}$ concentrations, but with improved EDBs the average results gave an approximately 12% overestimation in comparison with measured values in 2017. Beside that, it should also

be pointed out that measured $PM_{2.5}$ concentrations from Station 1 have substantially decreased when comparing the 2008/2009 and 2017 yearly average concentrations (roughly from 12 to 8 μg/m^3). With improved calculation, the yearly average $PM_{2.5}$ concentration in 2008 (including background concentration similar to Paper I) at the Station 1 was 9.2 μg/m^3 (4.2 μg/m^3 excluding natural background), whereas in Paper I it was assumed to be 17.1 μg/m^3 (10.8 μg/m^3 excluding natural background). The measured $PM_{2.5}$ concentration in 2008 was 12.6 μg/m^3, which may give the impression that by using improved EDBs, the model even underestimates the results, but it has to be taken into account that $PM_{2.5}$ measurements have been taken in Station 1 since August 2008. Thus, it can be assumed that improved EDBs are somewhat improving the health impact assessments. On the other hand, as the knowledge about the chemical composition of particles has been risen during the past years, it must be taken into account that $PM_{2.5}$ may contain a much higher concentration of toxic compounds, as shown from the high levels of eBC and B(a)P measured in Tartu, which are much higher than the results measured in the western part of Europe and Scandinavia (EEA, 2018a). Therefore, further research regarding particle toxicity and their role in public health impacts, is needed.

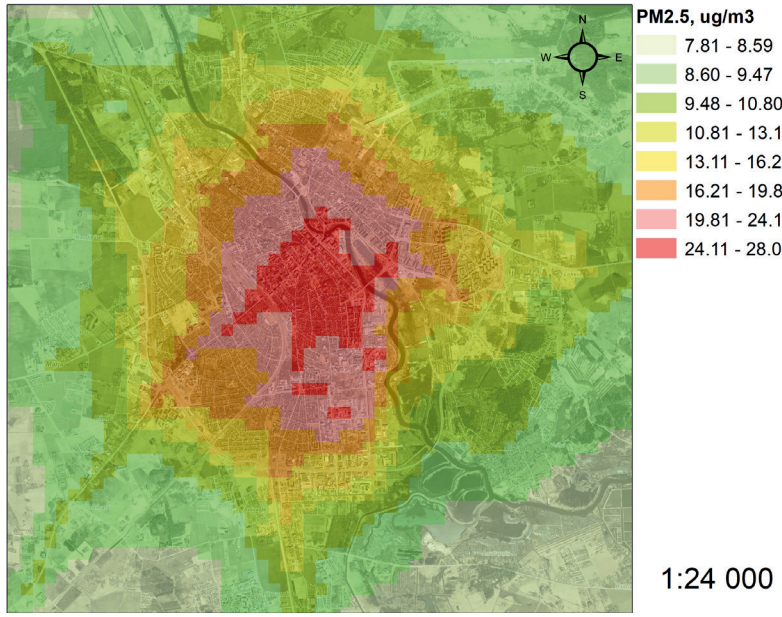

Figure 28. Modelled annual average concentration of $PM_{2.5}$ in Tartu in 2008 (based on Paper I data)

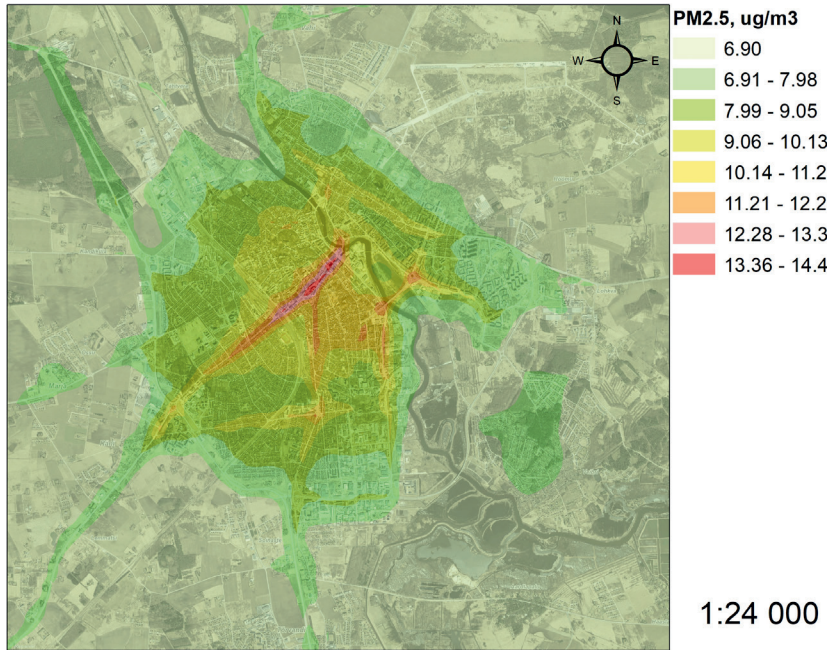

Figure 29. Modelled annual average concentration of $PM_{2.5}$ in Tartu in 2008 with improved input data from Paper II, IV and V

7. CONCLUSIONS

There is substantial exposure to coarse particles (PM_{10}) and fine particles ($PM_{2.5}$) in major Estonian cities that cause a considerable amount of health effects, mainly in the form of cardiovascular and respiratory diseases. Local heating and traffic remain the most significant factors contributing to air quality degradation that results in adverse health effects.

In the current thesis, by conducting several experiments, we obtained updated emission factors of residential wood and waste burning, as well as non-exhaust-related emissions from traffic and livestock farming, which can be used in national emission inventories and air-quality modelling.

Using the source apportionment technique (ME-2 analysis in combination with NR-$PM_{1.0}$ data from Q-ACSM and eBC data from aethalometer), we could see that residential heating contributes to around 20% of the total $PM_{2.5}$ concentration in Tartu, which is representative of a typical Estonian town. In the experiments it appeared that residential wood burning together with waste is a much larger source of particles, including toxic pollutants like PCDD/F, PAH and HCB, compared to burning purely wooden logs in domestic heaters, thus this should be taken into account in further emission inventories and in other relevant impact assessment studies.

In the current thesis, the air quality modelling approach with two waste burning scenarios was applied–wherein first it was assumed that 2% of the population regularly burns burnable waste in their household appliances (2% MSW scenario) and in the second scenario it was assumed that 45% of the population burns some burnable waste from time to time (45% MSW scenario). In most cases, the 45% MSW scenario largely overestimates $PM_{2.5}$ concentrations in comparison with measured $PM_{2.5}$ values, whereas the 2% MSW scenario generally correlated well with the measured values. Thus it can be assumed that a maximum of 2% of the population living in residential areas in Tartu and using heaters or stoves for heating and cooking purposes might burn some household waste. Even this share of the total population is small, during our experiments we noticed remarkable high toxic compound emissions in comparison

with clean wood experiments. Thus public awareness about the negative impacts of waste burning should be raised. Further research regarding particle toxicity and its role in public health is needed.

The previous model overestimated around 22% of measured $PM_{2.5}$ concentrations, but with improved EDBs the average results gave around a 10% improvement in comparison with measured and modelled $PM_{2.5}$ yearly average values. Thus, further improvements regarding important particle sources and their emissions in cities are needed and, of primary importance, EDB regarding household insulation data and emission dynamics should be improved.

The traffic non-exhaust emission measurements with the developed REAL system showed that it can adequately evaluate PM emissions using different tyre types. Test measurements identified a significant association between vehicle speed, tyre type and PM_{10} emission. The PM_{10} emissions are greatest with studded tyres at speeds above 50 km/h.

The agricultural NH_3 and PM yearly emissions based on retrieved emission factors from this study, were generally comparable to the official emission report results. PM emissions from the dairy cowsheds are negligible and their direct impact on Tartu air quality was minor. Nevertheless other studies are showing that NH_3 emissions are affecting ecosystems and contribute considerably to secondary particle formation, although during this thesis this was not seen.

Biomass burning from the residential sector is one the most important influences on air quality in a typical Estonian town, as was shown in this thesis where Tartu was chosen as a representative example. Thus, further improvements regarding the update and revision of EF and databases are needed, as the precision of those measurements has a direct effect on health impact assessments.

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SUMMARY IN ESTONIAN

Sissejuhatus

Õhusaaste on maailmas muutunud üheks tähtsamaks enneaegse suremuse põhjustajaks (OECD, 2012). Eeldatakse, et õhusaaste (välis- ja siseõhus) tagajärjel sureb igal aastal enneaegselt umbes 6 miljonit inimest (Landrigan *et al.*, 2018). Õhusaaste põhjustatud tervisele toimivaid olulisemaid mõjureid on PM_{10} (peenosakesed) ja $PM_{2.5}$ (eriti peened osakesed) sisaldused õhus, mida peetakse tervise hindamise indikaatorühendiks (Burnett *et al.*, 2014). Vaatamata sellele, et Euroopa Liidus (EL) kehtivad PM_{10} ja $PM_{2.5}$ välisõhu piirväärtused, ületatakse neid paljudes EL-i liikmesriikides sageli ning seetõttu mõjutab see suuresti rahvatervist (EEA, 2018a). Osakeste negatiivsed mõjud on enamasti seotud krooniliste südame- ja veresoonkonna- ning hingamisteede haigustega (WHO, 2013). Euroopa linnapiirkondades domineerivad peamiste õhusaasteallikatena biomassi kasutamine kodumajapidamiste kütmisel, maanteetransport, tööstuslikud ja põllumajanduslikud heiteallikad. Kodumajapidamistes kütuste põletamine domineerib PM_{10} ja $PM_{2.5}$ heitkogustes ning alates 2003. aastast on selle valdkonna heitkogused suurenenud vastavalt 13% ja 11% (EEA, 2014).

Biomassi kasutamine on tähtis taastuvenergia allikas, mida on soositud tänu kliimapoliitikale, mille eesmärk on vähendada inimtekkelisi süsinikdioksiidi heitkoguseid, kuid teisest küljest on kasvanud osakeste (PM), polütsükliliste aromaatsete süsivesinike (PAH), polüklooritud dibensodioksiinide ja- furaanide (PCDD/F) ja heksaklorobenseeni (HCB) heitkogused kodumajapidamiste sektorist (EEA, 2014). Biomassi suurenenud kasutamine võib kaudselt mõjutada maakasutust ja biogeensete lenduvate orgaaniliste ühendite heitkoguseid (Maas ja Grennfelt, 2016). Hinnanguliselt põhjustab puidu ja kivisöega elamute kütmine EL-is 61 000 enneaegset surma aastas (Chafe *et al.*, 2015). Kesk- ja Ida-Euroopas moodustab biomassi põletamine ligikaudu 32% summaarsest $PM_{2.5}$ heitkogusest (Karagulian *et al.*, 2015). Eestis tekib kodumajapidamiste kütteseadmetes biomassi põletamise tagajärjel 37% $PM_{2.5}$-st, 44% tahmast (BC), 46% PAH-st, 22,5% PCDD/F-ist ja 60% HCB-st (EEEA, 2018a). Enamasti eeldatakse et eramute kütmisel kasutatakse vaid puhast biomassi, kuid samas näitavad erinevad uuringud, et peale selle võidakse põletada ka olmejäätmeid. Jäätmete

põletamine eramutes kujutab endast märkimisväärset õhukvaliteedi mõjutajat ja tähtsat orgaanilise PM-i allikat (Mohr *et al.*, 2009). Olmejäätmete põletamine kodumajapidamiste ahjudes võib vähendada põlemisprotsessi efektiivsust (Moran *et al.*, 2009) ja põhjustada toksiliste saasteainete heidete suurenemist (Edo *et al.*, 2018; Hedman *et al.*, 2006). Samas napib kvantitatiivseid andmeid sellise tegevuse kohta, kuid võib eeldada, et põletamine on erineval tasemel levinud kogu maailmas, samas teave täpsete heitkoguste kohta on puudulik (Kupri *et al.*, 2018; Mohr *et al.*, 2009; Wiedinmyer *et al.*, 2014). Seetõttu on kodumajapidamiste riigispetsiifiliste PM-i eriheidete määramine kriitilise tähtsusega.

Liiklus tekitab peale heitgaaside ka saasteaineid, mis ei ole otseselt seotud kütuse põletamisega, nagu piduriketaste, rehvide ja teekatte kulumine, mida tähistatakse PM-i resuspensioonina (Hak *et al.*, 2009). Põhjamaades, sh Eestis, on laialt kasutusel naastrehvid, mis on talveperioodil liiklusohutuse seisukohast väga tähtsad, kuid suurendavad selles sektoris märkimisväärselt osakeste heitkoguseid. On leitud, et liiklussektoris on sõidukite heitgaaside heitkogused langustrendis (Kousoulidou *et al.*, 2008; Rexeis ja Hausberger, 2009). Samas võib eeldada, et sõiduki kuludetailide ja teekatte kulumisest (PM-i resuspensioon) pärinevate PM_{10} osakaal suureneb. Paljud EL-i liikmesriigid ei raporteeri oma PM-i resuspensiooni heitkoguseid õhusaasteainete inventuuride raames ja seda peetakse üheks peamiseks põhjuseks, miks õhukvaliteedi mudelid PM_{10} kontsentratsiooni alahindavad (Amato *et al.*, 2014).

Põllumajandussektor emiteerib Euroopa Liidus enamiku (92%) ammoniaagi (NH_3) heitkogustest ning 15% PM_{10}-st ja 4% $PM_{2.5}$-st (EEA, 2018b). Ajavahemikul 2013–2016 kasvasid NH_3 heitkogused põllumajandussektoris ligikaudu 3% (EEA, 2018b) ja need mõjutavad endiselt märkimisväärselt õhukvaliteeti (Chandrappa ja Chandra Kulshrestha, 2016). NH_3 mõjutab muu hulgas ökosüsteeme lämmastikusaaste, hapestumise ja eutrofeerumisega ning lisaks on NH_3 tähtis eeldusaine sekundaarsete osakeste tekkeprotsessis (Bluteau *et al.*, 2009; CambraLópez *et al.*, 2010). Hiljutised uuringud on näidanud, et loomakasvatus mõjutab $PM_{2.5}$ sisaldust välisõhus, mis on täheldatav sekundaarsete anorgaaniliste aerosoolide, sealhulgas ammooniumsulfaadi ja ammooniumnitraadi sisalduse suurenemise tõttu (Bauer *et al.*, 2016; Brunekreef *et al.*, 2015; Lelieveld *et al.*, 2015). Seetõttu on tähtis hinnata põllumajandusest tulenevate heitkoguste mõju õhukvaliteedile.

Saasteainete heitkoguste hindamiseks kasutatakse sageli heitkoguste inventuure üleilmsel või kohalikul tasandil. Heitkoguste inventuurides hinnatakse saasteallika heitkoguseid enamasti meetoditega, mis põhinevad suuresti eelnevalt määratletud valdkonna- ja allikaspetsiifilistel eriheidetel (EF), mis põhinevad enamasti saasteallikate heitkoguste mõõtmisel ning sõltuvad erinevatest teguritest, näiteks põletatud kütuse kogusest ja kvaliteedist (Seinfeld ja Pandis, 2006). Heitkoguste inventuuriandmeid on võimalik kasutada õhusaasteainete hajumismudelites, mis võimaldavad hinnata erinevate saasteallikate mõju õhukvaliteedile kohalikul, piirkondlikul või üleilmsel tasandil (Fairmode, 2010). Samas sõltub tulemuste kvaliteet otseselt sisendandmete kvaliteedist, näiteks kasutatud EF-ist ja kasutatud tegevusandmetest.

Eesmärk ja hüpoteesid

Töö põhieesmärk on hinnata tähtsamate antropogeensete saasteallikate PM heitkoguseid kodumajapidamiste kütmise tulemusena, PM-i resuspensiooni teekatetel ning PM-i ja oluliste PM-i eeldusainete kvantifitseerimist veisekasvatusest, sest PM halvendab märkimisväärselt õhukvaliteeti nii Euroopas kui ka Eestis.

Hüpoteesid

1. Õhukvaliteedi modelleerimise tulemuste ja tervisemõju hindamise määramatus sõltub eelkõige õhusaaste heitkoguste andmebaaside andmete kvaliteedist.

2. Kodumajapidamistes kasutatava puidu põletamisel, maanteetranspordi PM-i resuspensioonil ja loomakasvatuse heitkogustel on linnade õhukvaliteedile märkimisväärne mõju.

Töö konkreetsed eesmärgid olid järgmised.

1. Määrata PM–ist tuleneva õhusaaste tervisemõjud Eesti suuremates linnades vaikeväärtusena juhendmaterjalist (mitte-riigispetsiifiliste, Euroopa keskmised) leitavate PM-i eriheidete alusel.

2. Täpsustada eramute kütmise, PM-i resuspensiooni ja loomakasvatuse riigispetsiifilised eriheited.

3. Valideerida mõõdetud eriheited, kasutades selleks õhusaasteainete modelleerimisetehnikaid, ning hinnata andmete kvaliteeti õhusaasteainete heitkoguste inventuuri ja mõjuhinnangute kontekstis.

Metoodika

Doktoritöö esimeses etapis leiti õhusaaste võimalik mõju tervisele. Selleks modelleeriti Euroopa keskmisi eriheiteid (mitte-riigispetsiifilised) kasutades õhusaaste $PM_{2.5}$ ja PM_{10} sisaldus Eesti suuremates linnades ning elanikkonna paiknemise kaudu leiti rahvastiku keskmine kokkupuude õhusaastega. Tervisemõju hindamise metoodikat kasutades leiti tulenevalt õhusaastega kokkupuutest, käesoleva hetke suremuse ja haigestumuse tasemest ning läbi viidud epidemioloogilistest uuringutest leitud annuse-vastuse seostest eeldatav varajaste surmade ja haigestumiste arv (I artikkel).

Seejärel tehti puidu ja olmejäätmete koospõletamise katsed Eesti Keskkonnauuringute Keskuse ahjulaboris, kasutades Eestis laialt levinud umbkoldega pottsepaahju. Katsete käigus mõõdeti erinevate saasteainete (sh PM, PCDD/F, PAH, HCB) kontsentratsioonid ning arvutati vastav EF. Kütusesegude koostamisel lähtuti koduahjudes põletamiseks sobivate jäätmete osakaalust jäätmeinventuurides ja erinevates uuringutes toodud näitajatest (II artikkel).

PM-i resuspensiooni mõõtmiseks liikluses konstrueeriti mobiilne PM-i resuspensiooni mõõtelabor REAL (*Road Emission Aerosol Laboratory*), mis võimaldab mõõtmisi erinevate sõidukite ja rehvitüüpidega. Antud doktoritöö raames tehti mõõtmised naast-, lamell- ja suverehvidega, eesmärgiga hinnata erinevat tüüpi rehvide kasutamisel tekkiva PM_{10} heitkoguseid. PM-i resuspensiooni EF-i valideerimiseks kasutati III artiklis toodud PM_{10} eriheidet koos Airviro süsteemis oleva Gaussi algoritmil põhineva resuspensioonimudeliga Omstedti jt (2005) kirjelduse kohaselt (III artikkel).

Veisekasvatuses korraldati kaks kampaaniat vabapidamisel lüpsilautades. Esimese mõõtekampaania raames (IV artikkel) keskenduti peamiselt PM-i ja NH_3 sisalduse mõõtmisele vabapidamisel laudahoonetes üheksas lüpsifarmis. Teise mõõtekampaania käigus (V artikkel) keskenduti peamiselt PM-i erinevate fraktsioonide keemilise koostise määramisele vabapidamisel lüpsilauda siseõhus. Loomakasvatuse käigus tekkinud

heitkoguste andmebaasi koostamisel lähtuti loomakasvatushoonete asukoha ja loomade arvu määramisel Põllumajanduse Registrite ja Informatsiooni Amet (PRIA) andmebaasist. Kasutades IV ja V artiklist saadud tulemusi, arvutati PM_{10}, $PM_{2.5}$ ning NH_3 heitkogused iga objekti kohta, kasutades sarnast lähenemist, nagu on kirjeldanud Oravas (2015).

Selleks, et hinnata mõõtmise teel määratud eriheidete esinduslikkust, kasutati doktoritöö raames leitud EF-i saasteainete heitkoguste andmebaaside koostamisel, seejärel tehti õhukvaliteedi modelleerimised ning võrreldi modelleerimistulemusi välisõhu seirejaamade mõõtetulemustega. Käesolevas töös valiti EF-i valideerimispiirkonnaks Tartu linn. Õhukvaliteedi hajumisarvutuste jaoks koostati kohtkütte, liikluse resuspensiooni ja loomakasvatuse saasteallikate heitkoguste andmebaasid ning lisaks kasutati liikluse heitgaaside ja tööstuslike heitkoguste andmebaase, kus määratleti saasteallikate asukohad ning saasteainete hetkelised heitkogused (g/s PM_{10}, $PM_{2.5}$ ja lisaks NH_3 loomakasvatuses) iga heiteallika kohta (joonis 3). Iga saasteallika kategooria kohta tehti õhukvaliteedi hajumisarvutused Airviro süsteemis oleva Euleri advektsiooni-difusiooni hajumismudeliga ühetunnise sammuga vastava perioodi kohta (2014. a talv-kevad, 2016./17. a talv-kevad ja 2017. a terve aasta). $PM_{2.5}$ taustakontsentratsioonidena kasutati Saarejärve taustaseirejaama andmeid. Seejärel tulemused summeeriti ja mõõdetud tulemusi võrreldi Tartu õhukvaliteedi seirejaama andmetega (jaam 1) ning kolme teise seirejaama tulemusega (joonis 3). Veel kasutati modelleeritud kohtkütte osakaalu hindamiseks Kalevi seirejaamas mõõdetud $PM_{1.0}$ ($NRPM_{1.0}$, $\mu g/m^3$) ja eBC massikontsentratsioone ($PM_{1.0}$, $\mu g/m^3$), kasutades reaalaja aerosoolmassispektromeetrit (Quadrupol Aerosol Chemical Speciation Monitor, Q-ACSM, Aerodyne Research Inc.) ning seitsme lainepikkusega etalomeetrit AE-33 (Magee Scientific Inc.).

Antud dissertatsiooni raames tehti kohtkütte heitkoguste arvutused kahe stsenaariumiga. Esimesel juhul (45% MSW stsenaarium, ligikaudu 800 tonni põletatavaid olmejäätmeid aastas Tartu kohta) eeldati, et 45% elanikkonnast põletab aeg-ajalt mõningaid olmejäätmeid (EEEA, 2018. a). Teisel juhul (2% MSW stsenaarium, ligikaudu 35 tonni põletatavaid olmejäätmeid aastas Tartu kohta) eeldati, et maksimaalselt 2% elanikkonnast põletab olmejäätmeid regulaarselt (NIR, 2018).

Tulemused

Algsete (I artikkel) õhukvaliteedi modelleerimistulemuste põhjal eristuvad kohalike küttesüsteemidega piirkonnad selgelt suurema PM-i kontsentratsiooniga aladena. Suuremat PM-i kontsentratsiooni täheldati ka tiheda liiklusega tänavate piirkonnas. Väiksemat sisaldust täheldati linna elamupiirkondades, kus rahvastikutihedus oli suhteliselt väike.

Kokkupuude $PM_{2.5}$-ga viies uuritud linnas võib põhjustada keskmiselt 462 enneaegset surmajuhtu aastas, mis vastab 6034-le kaotatud eluaastale. Näiteks Tallinnas lüheneb oodatav eluiga õhusaaste tõttu keskmiselt 0,64 eluaastat ja Tartus 0,68 eluaastat (I artikkel). Peale selle leiti, et suurem osa õhusaaste väliskuludest on seotud pikaajalise mõjuga suremusele ja enneaegsete surmade tõttu kaotatud eluaastatele. Aastane õhusaaste väliskulu uuritud linnades küündib keskmiselt 270 miljoni euroni (95% CI 190–350).

Puidu ja olmejäätmete põletuskatsetes (II artikkel) oli mõõdetud suitsugaaside $PM_{2.5}$ keskmine kontsentratsioon 929,5 mg/Nm^3 (95% CI 560,7–1298,2) (13% O_2). Toksiliste ühendite, nagu PCDD/F-i puhul tuvastati, et katsete ajal olid PCDD/F-i keskmised kontsentratsioonid vahemikus 0,0116–0,1550 ng I-TEQ Nm^3 (11%, O_2), mis on teatud katsete puhul isegi suuremad kui jäätmepõletusetehastele seatud korstnasisesed piirväärtused (0,1 ng I-TEQ Nm^3, 11% O_2) (IED, 2010).

PM-i resuspensiooni mõõtmistulemuste puhul selgus (III artikkel), et suurimad PM_{10} EF-id saadi naastrehvide kasutamisel ning seda sõiduki liikumiskiirusel alla ja üle 50 km/h. Sõiduki liikumiskiiruse ja PM_{10} EF-i vahel valitses tugev seos (joonis 9). Suurem kontsentratsioon naastrehvide kasutamise korral on tingitud peamiselt naastrehvide suuremast abrasiivsusest teekatte suhtes ning suurem sõidukiirus tingib PM-i suurema lenduvuse teekatte pinnalt.

Veisekasvatuse puhul täheldati sooja- ja külmaperioodil selget varieeruvust mõõdetud kontsentratsioonides. Ööpäeva keskmine $PM_{2.5}$ ja PM_{10} heitkogus oli vastavalt 0,19 ±0,33 ja 0,36 ±0,48 grammi loomühiku kohta ööpäevas (g/LU/d). PM-i heitkogused olid külmema perioodi jooksul suuremad võrreldes soojema perioodiga. Veiselautades mõõdetud PM-i sisaldust mõjutasid talve- ja kevadhooajal suurel määral ka muud saasteallikad, nagu kodumajapidamistes puidu põletamine

(suurenenud K^+ sisaldus) ja piirkondlik saaste (suurenenud SO_4^{2-} sisaldus) (V artikkel).

Õhukvaliteedi täpsustatud modelleerimine tehti Tartu linnapiirkonnas ja sellest nähtub, et kõige saastunum piirkond asub Tartu kesklinnas ja Riia tänava piirkonnas, kus modelleeritud tulemused olid vahemikus 16–32 $\mu g/m^3$ 2% MSW ja 45% MSW stsenaariumi kohaselt. Üldiselt leiti tugev korrelatsioon 2% MSW stsenaariumi ja mõõdetud tulemuste vahel ning täheldati tugevat korrelatsiooni ($r > 0{,}500$) mõõdetud ja modelleeritud $PM_{2.5}$ väärtuste vahel 1., 2. ning 4. seirejaamas (tabel 1).

2016./17. a küttehooajal tuvastati faktoranalüüsi käigus viis peamist õhusaate tegurit Q-ACSM-i mõõtetulemuste järgi (joonis 14). Massi-laengu (m/z) suhte põhjal oli võimalik eristada järgmisi tegureid: biomassi põletamisest pärinev orgaaniline PM (BBOA), värskeid süsivesinikke sisaldav orgaaniline PM (HOA, mis on peamiselt seotud liikluse heitgaasidega), toiduvalmistamisest pärinev orgaaniline PM (COA), poollenduv oksüdeerunud orgaaniline PM (SV-OOA) ja vähese lenduvusega oksüdeerunud orgaaniline PM (LV-OOA).

PM-i resuspensioon põhjustab enamasti jämedama PM-i ($PM_{2.5–10}$) kontsentratsiooni suurenemist, seetõttu võrreldi 1. seirejaamas mõõdetud $PM_{2.5–10}$ sisaldust modelleeritud $PM_{2.5–10}$ kontsentratsiooniga 2014. aasta jooksul (joonis 18). Tehti modelleerimised nii naastrehvide EF-i (64 mg/vkm, III artikkel) kui ka välisõhu mõõtetulemuste põhjal konstrueeritud EF-iga (460 mg/vkm), kuid kummalgi juhul ei järginud modelleeritud sisaldus mõõdetud $PM_{2.5–10}$ sisaldust. Suurim erinevus tuleb välja kevadperioodil, kui mõõtetulemused näitavad suurt $PM_{2.5–10}$ kontsentratsiooni, samas ei suuda mudel sarnast kevadist piiki korrektselt välja tuua (joonis 18).

Kuna loomakasvatuse otsene mõju primaarsete PM-i heitkoguste kaudu Tartu õhukvaliteedile on marginaalne – seda peamiselt tänu PM-i sekundaarsele päritolule antud sektoris – kasutati mõõdetud EF-i, et arvutada välja kogu riigi veisekasvatuse PM-i ja NH_3 aastane heitkogus ning võrrelda seda ametliku õhusaasteainete heitkoguste inventuuri väärtustega. Eesti riikliku õhusaasteainete heitkoguste inventuuri andmete kohaselt emiteerisid lüpsilehmad 2015. aastal vastavalt 3,33; 0,023 ja 0,035 kilotonni (kt) NH_3, $PM_{2.5}$ ja PM_{10}. Kui võtta aluseks käesoleva dissertatsiooni käigus mõõdetud eriheited (V artikkel), siis

olid NH_3, $PM_{2.5}$ ja PM_{10} aastased heitkogused vastavalt 1,82; 0,019 ja 0,036 kt, mis on samas suurusjärgus nagu riiklikus inventuuris arvutatud heitkogused.

Diskussioon ja kokkuvõte

Käesoleva doktoritöö raames tuvastati, et EF-i täpsus mõjutab suurel määral välisõhu modelleerimistulemusi, millest omakorda sõltub tervisemõjude hinnangu täpsus. Sektorite osakaalu hindamine vastavate markerite kaudu võimaldas hinnata osakaalu suurust $PM_{2.5}$ kogumassist ning selle põhjal võib väita, et Tartu linnas mõjutavad õhukvaliteeti enim kohtküte ja liiklus, samas kui loomakasvatuse otsene mõju on marginaalne, sekundaarsete osakeste mõju vajab aga edasist uurimist.

PM-ist tuleneva õhusaaste tervisemõjude hindamine viies Eesti suuremas linnas näitas, et välisõhus sisalduv PM võib lühendada eluiga keskmiselt kuni 13 kuud, suurim mõju esineb linnakeskustes või suurtes kohtküttega eramupiirkondades (I artikkel). PM-iga kaasnevast saastest tingitud enneaegse suremusega seotud majanduslike kulude hinnang oli Tallinnas, Tartus, Kohtla-Järvel, Narvas ja Pärnus keskmiselt 270 miljonit eurot aastas. See vastab hinnanguliselt kolmele protsendile linnade SKP-st.

Antud doktoritöö käigus leiti, et halupuidu ja olmejäätmete põletuskatsete ajal oli $PM_{2.5}$ EF keskmiselt 1027,33 mg/MJ (II artikkel), mis on ligikaudu neli korda suurem võrreldes puhta puidu keskmise $PM_{2.5}$ EF-iga vanemat tüüpi umbkoldega ahju puhul (Teinemaa *et al.* , 2013) ja ligikaudu 43 korda suurem võrreldes puhta puidu keskmise $PM_{2.5}$ EF-iga uuemat tüüpi pottsepaahju puhul (Maasikmets *et al.*, 2015b). Toksiliste ühendite, nagu PCDD/F-i keskmine kontsentratsioon oli katsete ajal sarnane kontsentratsiooniga, mis kehtib jäätmepõletustehaste korstnasisese piirväärtusena. Seejuures tuleb arvestada, et see piirväärtus on kehtestatud suurtele jäätmepõletustehastele (näiteks Iru jäätmepõletustehas Eestis), kus heitkoguseid kontrollitakse ja jälgitakse korrapäraselt. Meie mõõtetulemused näitasid, et kodumajapidamiste küttekolded võivad olla märkimisväärsed toksiliste ühendite saasteallikad ja toksiliste ühendite sisaldus kasvab märkimisväärselt, kui peale puidu põletatakse ka olmejäätmeid.

Eesti õhusaasteainete inventuuri andmetel moodustasid PM-i resuspensiooni heitkogused 2014. aastal 49,6% kogu liiklusega seotud PM_{10} heitkogustest (EEEA, 2018b), mis on võrreldav teiste EL-i riikidega (Denier van der Gon *et al.*, 2018). Mõõdetud PM-i resuspensiooni EF-i põhjal arvutati Eestile PM-i resuspensiooni heitkogused. Kui võrrelda neid ametlike inventuuriandmetega, ilmneb, et ametlikult on heitkogused mõnevõrra suuremad (254 *vs.* 224 t/a 2010. aastal), kuid üldiselt on tulemused võrreldavad (joonis 20).

2% MSW stsenaariumi tulemused olid enamasti tugevas korrelatsioonis mõõdetud väärtustega, kuigi ka see stsenaarium ülehindas aasta keskmist kontsentratsiooni ligikaudu 12% ja 2016./17. a kütmisperioodil ligikaudu 6% võrreldes mõõdetud kontsentratsioonidega (joonis 17 ja joonis 15). Q-ACSM-i ja etalomeetriga tehtud mõõtmiste põhjal leiti, et kuigi korrelatsioon modelleeritud 2% MSW stsenaariumi ja mõõdetud kontsentratsioonide vahel oli tugev, on modelleeritud tulemused mõnevõrra kõrgemad biomassi osakaalu osas, mis viitab sellele, et kohtkütte $PM_{2.5}$ tegelik EF võib see olla isegi mõnevõrra väiksem kui antud doktoritöö raames leitud kohtkütte kaalutud keskmine EF (joonis 5).

Doktoritöö raames kasutatud NR-$PM_{1.0}$ ja eBC tulemusi kasutati kohtküttest pärineva $PM_{2.5}$ osakaalu hindamisel. Saadud tulemuste põhjal võib järeldada, et tulemid on piisavalt usaldusväärsed ja leitud saasteallikate osakaalu põhjal on võimalik anda palju täpsemalt erinevaid hinnanguid, sh teha oluliselt täpsemat tervisemõjude analüüsi. Keskmiselt moodustas NR-$PM_{1.0}$ kogumassist orgaanika (OA) – 61,5%, millele järgnesid sulfaat (17,5%), nitraat (13,4%), ammoonium (6,2%) ja kloriid (1,5%). Tulemused on kooskõlas varasemate mõõtetulemustega (Elser *et al.*, 2016). Keskmine OA kontsentratsioon oli 2,18 $\mu g/m^3$, mis on võrreldav suurus modelleeritud tulemustega (Denier van der Gon *et al.*, 2015). NR-$PM_{1.0}$ ja eBC summeerimine suurendab nende osakaalu $PM_{2.5}$ kogumassist keskmiselt kuni 71,27% ning mõõdetud $PM_{2.5}$ ja NR-$PM_{1.0}$+eBC vahel esines tugev korrelatsioon ($r = 0,817$), mis on kooskõlas teiste tulemustega (Aurela *et al.*, 2015; Budisulistiorini *et al.*, 2014; Elser *et al.*, 2016).

Lisaks võrreldi I artiklis ka modelleerimistulemusi uuendatud heitkoguste andmebaaside tulemustega (joonis 28). Nendest nähtub, et uuendatud andmebaaside kasutamine näitas suuremat kokkulangevust mõõdetud ja modelleeritud $PM_{2.5}$ kontsentratsioonide vahel ning lisaks võimaldavad

uuendatud andmebaasid palju paremini eristada piirkondi, kus võib esineda $PM_{2.5}$ suurem kontsentratsioon (joonis 29). Kui varasema (I artikkel) modelleerimistulemuse puhul oli modelleerimistulemuse aasta keskmise kontsentratsiooni ülehindamine ligikaudu 22%, siis heitkoguste uuema andmebaasi puhul väheneb see 2017. aastal 12%-ni.

Võib eeldada, et heitkoguste uuendatud andmebaasid võimaldavad täpsemini hinnata ka $PM_{2.5}$-st lähtuvaid tervisemõjusid, kuid seejuures tuleb kindlasti arvestada $PM_{2.5}$ keemilist koostist, sest teave Tartu linna $PM_{2.5}$ keemilise koostise kohta on viimastel aastatel märkimisväärselt täienenud. Antud dissertatsiooni raames leiti, et keskmiselt moodustab kodumajapidamiste kütmisest pärinev $PM_{2.5}$ 20% summaarsest $PM_{2.5}$ kontsentratsioonist, kuid kütmisperioodil võib kohtkütte osakaal olla palju suurem. Peale selle võib kohtkütte piirkonna $PM_{2.5}$ olla märksa toksilisem, kui seni eeldatud, sest puidu ja olmejäätmete katsepõletamistega tuvastati, et olmejäätmete põletamisel kasvab märgatavalt toksiliste ühendite, nagu PCDD/F, PAH-i ja HCB sisaldus suitsugaasides. Seda kinnitavad omakorda ka välisõhu kvaliteedi mõõtmised Tartu linnas, mille raames on mõõdetud oluliselt kõrgemaid eBC ja B(a)P sisaldusi võrreldes näiteks Skandinaaviaga (EEA, 2018a). Kuna Tartus mõõdetud tulemustega sarnaseid $PM_{2.5}$ ja B(a)P tulemusi on mõõdetud ka teistes Eesti väikelinnades, siis võib eeldada, et taolised tingimused valitsevad ka mujal. Siiski on mõõtetulemused lünklikud ja vajaksid $PM_{2.5}$ keemilise sisalduse osas edasist uurimist. Sellest lähtuvalt on vaja lisauuringuid osakeste toksilisuse ja nende rolli kohta tervisemõju hindamisel.

AKNOWLEDGEMENTS

I would like to thank everybody who supported me while writing my doctoral thesis, especially my supervisor Erik Teinemaa, PhD, for helping me with the emission measurement preparation and data analysis. I also thank him for helping me come up with a topic and for helping me put this thesis together. Special thanks are due to him for being patient during this rather long 'journey' and for being always helpful and motivating during the whole process. I would also like to thank Associate Prof. Hans Orru for being my supervisor and for helping me with the finalization process of the thesis. I'm thankful to my supervisor Prof. Valdo Kuusemets, who was always helpful and reminded me about the final deadlines. I wish to express my gratitude to Dr. Veljo Kimmel for his valuable comments on my papers and thesis manuscript. Many thanks to Dr. Allan Kaasik, who was my guide during the livestock emission measurement campaigns.

I am thankful to the official reviewer of the thesis, Dr. Marko Kaasik from the University of Tartu, for reviewing and commenting on this thesis. I highly appreciate that Dr. Heikki Junninen from the University of Helsinki and University of Tartu has kindly promised to be my official opponent in the public examination of this thesis.

I am grateful to all my co-authors and to colleagues from the Estonian Environmental Research Centre, from the Estonian University of Life Sciences, from the University of Tartu and from the TALTECH, for their helpful co-operation during the work. I especially wish to thank all my colleagues and ex-colleagues at EERC - Keio, Aivo, Riina, Aser, Peeter, Arkadi, Katri, Kaisa, Maris, Hannes, Tarvo, Lehar, Stanislav, Krista, Laine and many more from the air department and from the laboratory, for creating a pleasant and inspiring work atmosphere. Special thanks goes to Hanna-Lii, who was always there and ready to 'jump in' during all experiments. I couldn't imagine having my thesis ready without using Airviro system, which makes working with measured and modelled data very easy – my special thanks goes to Pär and Lars from Apertum IT.

I'm thankful to people from the Ministry of Environment and from the Estonian Environment Agency, especially to Heidi, Marina, Kaidi, Reet, Natalija, Elo, Helen and Ardi for their advice and support during fruitful

discussions about the ‘right and wrong’ emission factors and about the future perspectives regarding air pollution mitigation measures.

Finally, I warmly thank my family for their loving patience and support throughout my thesis preparation–this has been long journey, but thanks to you, I had opportunity to finalize it.

Although the PhD journey has been rather long, it has showed me that it’s never too late to study and there is so much interesting to learn more about the life surrounding us, thus never give up on learning everyday something new!

I

PUBLICATIONS

Orru, H.; **Maasikmets, M.**; Lai, T.; Tamm, T.; Kaasik, M.; Kimmel, V.; Orru, K.; Merisalu, E.; Forsberg, B. (2011). Health impacts of particulate matter in five major Estonian towns: main sources of exposure and local differences. Air Quality, Atmosphere & Health, 4(3-4), 247–258.

Air Qual Atmos Health
DOI 10.1007/s11869-010-0075-6

Health impacts of particulate matter in five major Estonian towns: main sources of exposure and local differences

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Received: 3 December 2009 / Accepted: 26 May 2010

Abstract Particulate matter (PM) is the major air pollution problem with health impacts in Estonia. The prevailing sources of particles are traffic and local heating. In this study, we quantified the health effects of PM in neighbourhoods of five main cities with a health impact assessment (HIA) approach that uses information on exposure, baseline mortality/morbidity and exposure–response relationships from previous epidemiological studies. The exposure was defined as modelled $PM_{2.5}$ annual levels and daily averages of PM_{10} (monitoring data in Tallinn and Kohtla-Järve and modelled levels in Tartu, Narva and Pärnu). The modelled results were validated with data from monitoring stations and additional measuring programmes. The annual average concentration of $PM_{2.5}$ in the neighbourhoods studied varied from 7.6 to 23.6 μg m^{-3}. The analysis indicated that the exposure above natural background corresponds to 462 [95% confidence interval (CI) 120–815] premature deaths, resulting in 6,034 (95% CI 1,583–10,309) years of life lost per year. The average decrease in life-expectancy at birth per resident of Tallinn was estimated to be 0.63 (95% CI 0.16–1.08) years. In the polluted city centres, this average decrease may reach >1 year and in Pärnu, it may reach 0.95 year. However, in the least polluted neighbourhood, the decrease of life expectancy was only 0.17 years. In addition, 231 (95% CI 145–306) respiratory and 338 (95% CI 205–454) cardiovascular hospitalisations per year could be expected. The majority of the external costs are related to the long-term effects on mortality and amount to €270 (95% CI 190–350) million annually. In comparison, the costs of hospitalisations contribute just €1.1 (95% CI 0.6–1.6) million. The main differences in health impacts were mostly driven by differences in the pollution sources, the magnitude of such sources and distribution patterns in the atmosphere. The smallest health effects, with the exception of the green residential areas, were observed in the industrial cities Kohtla-Järve and Narva (due to the small share contributed by local residential heating and relatively little car traffic). However, it is questionable whether the mass of fine particles is the best indicator of air pollution risk in such areas.

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Published online: 11 June 2010

Keywords Health impact assessment · Air pollution · Particulate matter · Dispersion modelling · Traffic · Local heating · Costs

Introduction

Air pollution is one of the most salient issues in environmental health. The relationship between air pollution and human health is being intensively studied throughout the world; however, much remains to be understood. Even though air pollution levels have dropped in recent decades, air pollution remains a significant problem. One of the most important triggers of air pollution-related health effects is particulate matter (PM). PM consists of tiny particles of solid or liquid suspended in the air. Permitted values in PM_{10} (particles <10 μm in diameter) and $PM_{2.5}$ (<2.5 μm) are frequently exceeded in Europe (EEA 2009). Additionally, epidemiological studies have shown that health effects may even appear at lower levels than the current limit values (ERS, ISEE, ISEA 2006), and available data have not established firm threshold values (Chen and Kan 2008; Anderson 2009).

PM has been widely studied and is associated with numerous health outcomes either with short-term or long-term exposure. Many short-term exposure studies have reported on the relationship between PM and mortality and morbidity, and there have also been several meta-analyses of these studies, some of which have provided pooled effect estimates (Anderson et al. 2005). The relationships have also been found in multi-city studies (Katsouyanni et al. 2003; Dominici et al. 2005; Wong et al. 2008).

Long-term exposure to PM (years or decades) leads to chronic health problems, such as cardiovascular disease, cardiopulmonary disease and lung cancer. The association between particles and increased mortality has been shown in cohort studies conducted in the USA (Dockery et al. 1993; Pope et al. 1995; Abbey et al. 1999; McDonnell et al. 2000; Pope et al. 2002; Jerrett et al. 2005; Laden et al. 2006) and Europe (Hoek et al. 2002; Filleul et al. 2005; Gehring et al. 2006; Naess et al. 2007). However, the results of these studies are often dissimilar, most likely due to the use of different exposure metrics and slightly diverse endpoints. The main difference between U.S. and European studies is that North American studies tend to compare mortality or morbidity between communities rather than within communities (Brunekreef 2007).

It is believed that the negative effects of particles are mostly related to chronic cardiopulmonary diseases (Pope and Dockery 2006; Schwarze et al. 2006). PM together with its components [e.g. polycyclic aromatic hydrocarbons (PAH), volatile organic compounds (VOC)] are able to induce inflammatory processes and cause activation of redox mechanisms and oxidative stress (Nel 2005; Pope and Dockery 2006; Brook 2008).

The components and fractions of particulate pollutants related to adverse health effects are still not fully understood; therefore, particles are largely used as an indicator of toxic air pollutants in epidemiological studies. Still, many studies have shown that the smaller the PM size, the higher the toxicity through mechanisms related to oxidative stress and inflammation (Valavanidis et al. 2008). While these toxicological data are supported by the epidemiological findings (Kappos et al. 2004), a review of epidemiological studies has shown that there seems to be ambiguous health effects also resulting from the coarser particle mode, namely, $PM_{2.5–10}$ (Brunekreef and Forsberg 2005). According to these authors, acute exposure to coarse PM may be significantly associated with mortality and morbidity (especially respiratory hospital admissions). People with chronic diseases, such as asthma, chronic obstructive pulmonary disease, pneumonia, or other respiratory diseases, as well as patients with cardiovascular diseases, and diabetes are especially affected and can be defined as risk groups.

Different sources of particles

Estonia is an example of a transitional country, having regained its independence from the former Soviet Union only in 1991. The car fleet and main air pollution sources are currently relatively similar to those of other European countries, and especially similar to those of the Nordic countries (Orru et al. 2008). Traffic exhaust, the use of studded tires, and the intensive use of local heating by a large proportion of the population are considered to be the most problematic air pollution sources. In terms of pollutants, the relatively high levels of PM is of major concern (Urb et al. 2005; Kirso et al. 2006), similar to the situation in other European countries (Danielis 2006).

The health relevance of traffic-induced air pollution has been demonstrated in numerous studies on the associations between PM and acute respiratory illness, lung cancer, chronic respiratory, and cardiovascular diseases and cardiopulmonary mortality (WHO 2005b). While fine particles ($PM_{2.5}$) and ultrafine particles (UFP) are mainly generated by combustion from exhaust, non-exhaust particles (mainly $PM_{2.5–10}$) typically arise from abrasive sources, such as brake wear, tire wear and abrasion of the road surface (Thorpe and Harrison 2008). However, recent studies show that the use of studded tires contributes not only to PM_{10}, but also to $PM_{2.5}$ and likely also to PM_1 (Gustafsson et al. 2008).

Residential wood combustion is widely used for local heating in Estonia (Kaasik et al. 2007) and has been found to be a significant source of particulate pollutants in many European countries (McDonald et al. 2000; Hellén et al.

2008; Frey et al. 2009). Moreover, combustion emits PAH and monosaccharide anhydrides (levoglucosan and mannosan), which have been found to be higher in urban areas than in background sites (Glasius et al. 2008).

Industrial sources of air pollution include boiler houses, power plants, smelters and incinerators. In Eastern Europe (especially Russia), these have a very high public health relevance (Cara et al. 2007; Jedrychowski et al. 2007). In the Estonian setting, district heating is an important point source that influences the urban air quality in major cities. However, the health risks from boiler houses are much smaller than those from other particle sources (Orru et al. 2009b).

Risk assessments of air pollution

Risk assessment is an important tool used by researchers to estimate the increased risk of health problems in people exposed to different levels of particles. This approach combines the results of human exposure, baseline mortality or morbidity in the population and exposure–response (E–R) relationships from epidemiological studies. Health impact assessment (HIA) is a risk analysis tool by which a policy, programme or project may be evaluated based on its potential effects on the health and distribution of those effects in a population (Wismar et al. 2007). As such, PM effect estimates provides valuable information that can be used by policy-makers, for example to improve regulatory standards, reduce human exposure to toxic air pollutants, and decrease the risk of the public experiencing health problems.

According to the World Health Organisation (WHO; 2002), air pollution is responsible for 1.4% of all premature deaths and 0.8% of disability-adjusted life years globally. Exposure to outdoor air pollution accounts for approximately 2% of the global cardiopulmonary and 1% of the total respiratory disease burden (Cohen et al. 2004). Although the magnitude of the estimated increased risk does not appear to be extensive, the numbers of people affected are very large when extrapolated to the entire population that has been exposed (Chen et al. 2008). Moreover, public health effects can be substantial and costly, even in areas with relatively low levels of air pollution (Furberg et al. 2005).

Several HIAs focusing on particle effect in Europe have been published. One of the first studies (Künzli et al. 2000) estimated the impact of particulate pollutants in Austria, France and Switzerland. The authors found that PM causes 40,000 premature deaths, 25,000 new cases of chronic bronchitis and hundreds of thousands of chronic bronchitis episodes and asthma attacks each year. Other early HIAs have found that the lifespan of men in the Netherlands can be decreased by 1.5 years due to air pollution (Brunekreef 1997).

A recent large HIA included 23 European cities in the Apheis project (Boldo et al. 2006). This study showed that by reducing annual mean $PM_{2.5}$ concentrations to 15 μg m^{-3}, nearly 17,000 premature deaths could be avoided in the participating cities. Additionally, the average life expectancy at birth would increase by up to 2 years in more polluted cities (Boldo et al. 2006). The most recent large assessment from the USA found that a decrease in $PM_{2.5}$ annual mean concentrations by 10 μg m^{-3} corresponded with an estimated increase in mean life expectancy by 0.61 years (Pope et al. 2009).

If the $PM_{2.5}$ annual mean concentration remains <10 μg m^{-3} (WHO guidelines), the premature death rate would be reduced by 41 individuals per 100,000 population in the cities participating in the Apheis project (Ballester et al. 2008). Furthermore, if the agreed policies related to PM reductions were to be fulfilled, the average life expectancy in Europe would increase by 2.3 months by 2020 (WHO 2005a). Fine particles have been reported to have decrease the average life expectancy at birth by 8.6 months among all European Union (EU) citizens and to have been the cause of annual premature death amongst 348,000 people in Europe in 2000 (COMM 2005). Worldwide, the annual number of premature deaths due to outdoor $PM_{2.5}$ has been estimated at >800,000 (Cohen et al. 2004). A more recent study places this estimate at 3.5 million premature deaths from cardiopulmonary disease and 220,000 mortalities from lung cancer (Anenberg et al. 2010).

To a large extent, the adverse health effects stem from air masses originating in more polluted areas. Air pollution in Russia causes 87,000 deaths annually and comprises approximately 4% of Russia's total mortality (Golub and Strukova 2008). Estimates suggest that if the annual $PM_{2.5}$ level were to be lowered to 12 μg m^{-3} in Tokyo, Japan, the total mortality rate would decrease by 8% and 6,700 premature deaths would be prevented (Yorifuji et al. 2005). Forsberg et al. (2005) assessed that PM matter accounted for 4,700 premature deaths in Swedish cities and nearly 600 deaths in the countryside.

The negative effects of air pollution of public health have both direct and indirect costs to society. In the EU, the external annual costs of air pollution are estimated at between €50 and161 billion due to premature mortality and €29 billion from morbidity. This corresponds to more than 1% of the gross domestic product (GDP) of the EU (WHO 2005a). It is also important to note that the majority of the morbidity-related external costs from air pollution are related to the public health sector (years of life lost, YLL) and not to the health care sector (hospitalisations and medical care) (ExternE 2005). In the relatively more polluted countries of the world, such as China, health care costs associated with air pollution account for as much as 3.3% of the GDP (World Bank

2007). In Russia, these values are even higher (Golub and Strukova 2008).

An air pollution HIA has already been published on Tallinn (Orru et al. 2009c), but in the study reported here, we have expanded the analysis by adding four other towns with diverse characteristics. We also discuss the possible reasons for these differences among the cities and probable weaknesses of the HIA procedure.

Material and methods

Study sites

The study presented in this paper was performed in five major cities in Estonia: Tallinn, Tartu, Kohtla-Järve, Narva and Pärnu.

Tallinn, the largest city in Estonia and also its capital, is situated on the country's northern coast on the Gulf of Finland. The sources of air pollution in Tallinn are quite complex; however, traffic and local heating make significant contributions. Other contributors to increased emissions include the large number of cars in Tallinn that are more than 10 years old, with higher exhaust emission coefficients than newer vehicles, and the extensive use of wood stoves with low stacks for heating.

Tartu is the second largest city in Estonia and situated inland in a river valley. Similar to Tallinn, Tartu's street network capacity remains limited as the volume of traffic steadily increases; consequently, congestion is common during rush hours. Furthermore, because of domestic heating in the large number of small apartment houses, the proportion of emissions related to local heating in Tartu is even higher than that in Tallinn.

Kohtla-Järve and Narva are industrial cities, situated in the eastern part of Estonia. The main industries are related to oil shale, electricity generation and the production of fertilisers. The traffic flows are much less dense than those in Tallinn and Tartu, and the proportion of local heating is very low.

Pärnu is the fifth largest city in Estonia and is situated on the western coast on Pärnu Bay; the Pärnu River flows through the city.

Thus, all five cities differ not only in their pollution patterns, but also by their different distribution patterns of pollution, with two cities situated on relatively windy coasts and three cities situated inland to varying extents. In the summer, Pärnu is a popular vacation resort, and the traffic flows increase extensively during holiday seasons. Moreover, local heating is especially common in the central part of the city.

Methodological overview of health impact assessment

Our aim was to estimate the health impacts of particle emissions in Tallinn, Tartu, Kohtla-Järve, Narva and Pärnu. The population data for Tallinn were obtained from the Estonian Population Register in 2006 and was divided according to address and registration into the following age groups: 0–6, 7–17, 18–27, 28–37, 38–47, 48–57, 58–67, 68+ years. The population data for the other four cities are based on population count data in 2000 (age groups: 0–5, 6–10, 11–15, 16–20, 21–30, 31–40, 41–50, 51–64, 65+ years), which were available in 500 × 500-m grids in the cities. The citizens' residences were divided into neighbourhoods (regions with similar geographical and socio-economic patterns, among others, used in city planning and management) to identify site-specific exposure to air pollution and identify those areas with greatest risk. The age-structure of the population in these areas was also studied. Baseline total mortality data (A00–Y98), cardio-pulmonary mortality data for the sensitivity analysis (I10–I69, J00–J99) and data on hospitalisation due to cardiovascular (I00–I99) and respiratory cause (J00–J99) were retrieved from statistics for Estonia and from the Estonian Health Insurance Fund (EHIF) in 2006 and 2007.

The annual levels of $PM_{2.5}$ were modelled using AirViro, Web based environmental GIS tool, with a grid resolution of 200 × 200 m. AirViro, developed by The Swedish Meteorological and Hydrological Institute, uses data on emissions, measured levels from air pollution monitoring stations and meteorological variables from meteorological stations. These data are used to perform air pollution dispersion modelling and mapping. The average concentration of grid cells in a neighbourhood was assigned as the typical long-term exposure to all residents of that area. Short-term effects of air pollution were calculated using daily average concentrations of PM_{10} recorded by the monitoring stations in 2006 in Tallinn and in 2008 in Kohtla-Järve (measured by beta-attenuation analyzers; model FH-62; Thermo Andersen, Smyrna, GA). In Tartu, Narva and Pärnu, the daily PM_{10} concentrations were modelled for 2008, and the modelling results were validated with monitoring station data recorded in Tallinn and Kohtla-Järve (stations operated during the whole study period) and in Tartu and Narva (stations opened summer and fall 2008). For additional model validation, measuring campaigns were conducted in Tartu, Narva and Pärnu using FH 62-I-R β-radiation absorption equipment.

From the exposure assessment for the HIA calculation, we subtracted the natural background, as many experts believe that there are likely no effects below these levels. Moreover, we can only diminish the anthropogenic part of the particulate pollution, not the natural sources. As fine particles are not measured in Estonian rural areas, the annual concentration (approx. 5 μg^{-3}) in nearby areas of Helsinki was used as the natural background in Tartu, Kohtla-Järve, Narva and Pärnu (YTV 2008). However, as earlier modelling in Tallinn was based only on local

emission, the effects in Tallinn were calculated according to these modelled annual levels that were smaller by a natural background rather than from actual measured concentrations (Orru et al. 2009c).

For the mortality analysis, we used the following E–R relationship from previous studies: a total mortality increase of 6.2% [95% confidence interval (CI) 1.6–11%] per 10 μg m^{-3} increase of annual mean $PM_{2.5}$ concentration (Pope et al. 2002). For the sensitivity analysis, we used a cardiopulmonary mortality increase of 13% (95% CI 10–13%) per 10 μg m^{-3} increase of annual mean $PM_{2.5}$ concentration. We used an E–R relationship of 1.0114 per 10 μg m^{-3} increase of PM_{10} to calculate hospitalisations due to respiratory ailments (Atkinson et al. 2005). For cardiovascular hospitalisations, we used an E–R of 0.73% (95% CI 0.47–0.93%) as a weighted average based on the occurrence of cardiac and cerebrovascular admission with E–Rs from COMEAP meta-analysis. The cases of premature deaths were calculated in city districts (bigger city administrative region) in Tallinn and in neighbourhoods in other cities. For these calculations, the following equation was used:

$$\Delta Y = (Y_0 \times pop) \times (e^{\beta \times X} - 1)$$

where Y_0 is the baseline rate; *pop* is the number of exposed persons; β is the exposure–response relationship (relative risk); X is the estimated excess exposure.

The number of YLL and decrease in life expectancy were assessed using the WHO software programme AirQ 2.2.3 in all 142 neighbourhoods. The number of hospitalisations was determined with AirQ at different exposure intervals (10–19.9 μg m^{-3}, 20–29.9 μg m^{-3}, …) in Tallinn, Tartu, Kohtla-Järve, Narva, and Pärnu. For the calculation of short-term exposure effects, no effect was assumed below 10 μg m^{-3}.

The direct expenses related to morbidity were calculated using the costs of hospitalisation, while time on sick leave (data provided by EHIF) was used to calculate loss of labour input.

To determine the cost of premature deaths, the value of a life year was calculated based on the decrease of life expectancy (due to PM exposure) retrieved from the statistical value of life (equal to 120-fold the GDP per capita in a country). The methodology has been described in more detail by Orru et al. (2009c).

Results

Population and baseline mortality and morbidity

Altogether it was possible to define 650,225 air pollution-affected inhabitants: 388,964 in Tallinn, 101,192 in Tartu, 46,187 in Kohtla-Järve, 68,445 in Narva and 45,437 in Pärnu. All 142 neighbourhoods were different in terms of area, number of inhabitants, population density, main pollution sources and pollution concentrations. The main factors affecting the HIA results were exposure to particles, baseline mortality/morbidity and, to some extent, population age structure in the cities.

The mortality rates differed among the cities in different age groups. On average, the rates per 100,000 citizens per year were 1,136 cases in Tallinn, 1,037 in Tartu, 1,515 in Kohtla-Järve, 1,346 in Narva and 1,251 in Pärnu. The baseline annual hospitalisation rates were determined separately for cardiovascular and respiratory admissions using the same principles. The analysis showed that, on average, there were annually 6,204 and 2,765 hospital admissions for cardiovascular and respiratory health-related problems per 100,000 people in these cities.

Exposure to PM

In Tallinn and Tartu, the city centre and neighbourhoods with local heating could be clearly distinguished as areas with bigger exposure to fine particles (Fig. 1). Higher concentrations also appeared in residential areas close to busy streets. In Pärnu, all of the areas in the central part of city and close to the river valley appeared to have high values (neighbourhood average of up to 23.6 μg m^{-3}). The lower levels in Pärnu were notable in Raeküla and the southern part of Kesklinn, where blockhouses with central heating dominate. The lowest levels in these three cities appeared in residential areas located at the edges of the cities, where population density is relatively low (e.g. neighbourhood average in Ihaste was 7.6 μg m^{-3}; Fig. 1).

Of the five cities studied, the smallest levels were distinguished in Narva and Kohtla-Järve. Even though these are large industrial cities, the outdoor concentrations of particles in urban areas were not very high there. Somewhat higher levels appeared in the Ahtme mining area and the region near the Narva River; however these levels remained lower than those in the other three cities. Moreover, these cities have less traffic and local heating is very rare.

The daily averages of PM_{10} differed considerably among days and cities. The highest values were seen in Tallinn, where they reached up to 136 μg m^{-3}. The lowest concentrations—just few micrograms per cubic metre—were found on various days in different towns. However, the majority of the PM_{10} daily levels stayed between 10 and 30 μg m^{-3}.

The modelling results were validated with monitoring station data from Tallinn and Kohtla-Järve (stations were in operation during the whole study period), Tartu and Narva (stations opened in the summer and fall of 2008) and Pärnu

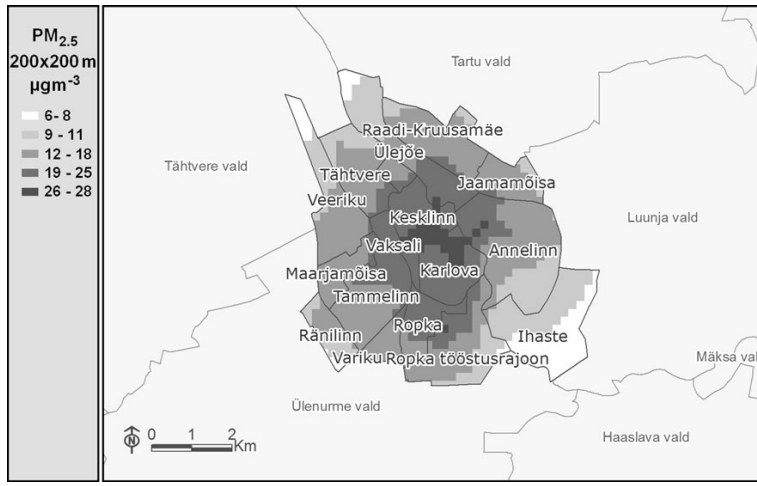

Fig. 1 Modelled annual average concentration of fine particles in Tartu

(mobile station in 2008).The average difference for all monitoring stations above the modelled PM levels over the measurement time was 22% (Table 1). In Tartu and Pärnu, the modelled levels were mostly higher than the measured levels, revealed that the emission databases for local heating are probably overestimated. In Kohtla-Järve and Narva, the measured values were higher than the modelled values, and we can assume that the emission databases are underestimated for these cities. The model validation in Tallinn has been discussed previously by Orru et al. (2009c). Even the agreements between the measured and modelled PM levels were imperfect; the model should satisfactorily represent the particle levels at different receptor points in the city as well.

Health effects and socioeconomic impacts

It was established that particulate pollutants cause on average of 462 premature deaths per year, corresponding to 6,034 YLL (Table 2). The greatest total loss (205–650 YLL) was expected in neighbourhoods with a large number of residents (>20,000), such as Mustamäe, Lilleküla, and Laagna in Tallinn, Annelinn in Tartu and Kesklinn in Pärnu (Fig. 2). This is likely to be reflected in the reduction of life expectancy by an average of 0.64 years in Tallinn, 0.68 years in Tartu and 0.95 years in Pärnu. In the city centres and in regions with extensive local heating, the life expectancy may be decreased by up to 1.2 years, whereas in the least polluted neighbourhoods, the decrease of life

Table 1 Annual average measured and modelled levels of particulates in the measuring stations and annual population average exposure to fine particles in five major Estonian cities

City	Modelled annual population average exposure to $PM_{2.5}$ (µg m^{-3})	Measuring station	Annual average levels (µg m^{-3})	
			Measured	Modelled
Tallinn	11.9[a]	Liivalaia PM_{10}	32.2	29.8[a]
		Rahu PM_{10}	25.7	14.7[a]
		Õismäe PM_{10}	22.6	18.2[a]
		Õismäe $PM_{2.5}$	11.6	9.1[a]
Tartu	10.8[a]	Kalevi $PM_{2.5}$	12.6	17.1
Kohtla-Järve	4.6[a]	Kalevi PM_{10}	18.7	12.2
Narva	7.5[a]	Kreenholmi $PM_{2.5}$	14.3	14.4
Pärnu	15.0[a]	Endla PM_{10}	36.7	49.8

PM, Particulate matter

[a] Excluding the natural background

Table 2 Annual effects due to exposure to PM in five major Estonian cities

City	Number of premature deaths		Years of life lost	Decrease in life expectancy (years)	Number of hospitalisations	
	Original calculation based on total mortality	Sensitivity analysis based on cardio-pulmonary mortality			Respiratory	Cardiovascular
Tallinn	296 (76–528)	295 (226–363)	3,859 (1023–6636)	0.64 (0.17–1.10)	71 (43–104)	204 (131–260)
Tartu	64 (17–111)	72 (55–88)	838 (221–1449)	0.68 (0.16–1.15)	71 (46–90)	58 (32–85)
Kohtla-Järve	18 (5–31)	19 (14–23)	257 (62–408)	0.35 (0.08–0.55)	19 (12–24)	16 (9–23)
Narva	37 (10–64)	42 (32–51)	534 (138–908)	0.51 (0.13–0.85)	32 (20–40)	33 (18–47)
Pärnu	47 (12–81)	49 (37–61)	546 (139–908)	0.95 (0.24–1.58)	38 (24–48)	27 (15–39)
Total	462 (120–815)	476 (365–586)	6,034 (1583–10309)	0.63 (0.16–1.08)	231 (145–306)	338 (205–454)

Values are given as the annual mean with the 95% confidence interval (CI) in parenthesis

expectancy remains around 0.3 years (Fig. 3). If the average number of YLL is divided by the number of premature deaths, the loss will be approximately 13 years among these individuals, indicating greater health impacts among risk groups. The risk groups include individuals with chronic respiratory and cardiovascular disease, among other diseases, and immunosuppressed persons who could live several years less due to outdoor air pollution exposure. Additionally, 231 (95% CI 145–306) respiratory and 338 (95% CI 205–454) cardiovascular hospitalisations could be expected annually as a consequence of short-term exposure to PM_{10} (Table 2).

Most of the external costs of air pollution are related to the long-term effects on mortality and years of life lost from premature deaths. Annually, this will add up to €270 (95% CI 190–350) million. Compared to losses from premature mortality, the costs of short-term exposure are small, €1.1 (95% CI 0.6–1.6) million, with the majority (>55%) being directly related to hospitalisations, and the rest to lost input to the national economy due to time spent on sick leave.

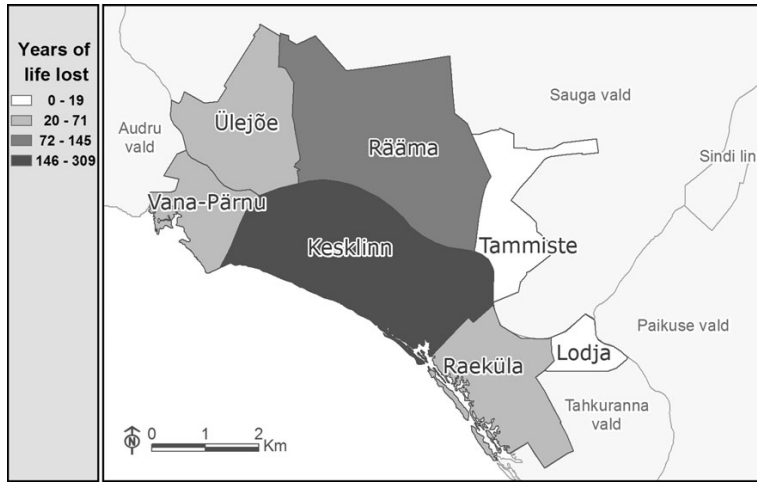

Fig. 2 Years of life lost in Pärnu neighbourhoods

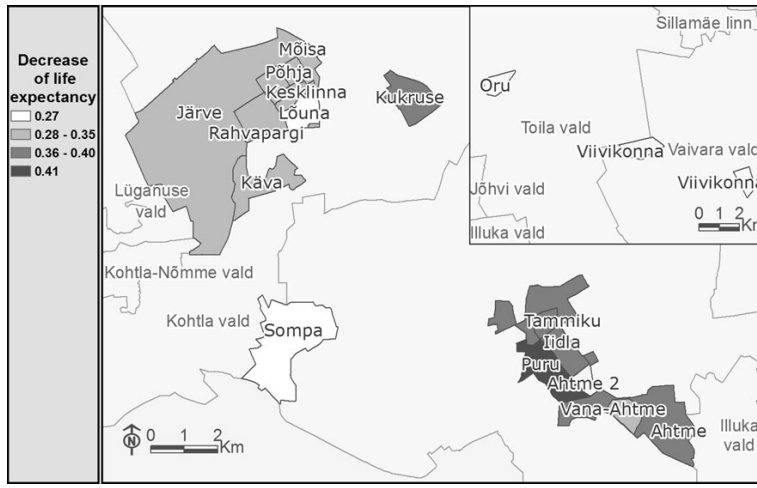

Fig. 3 Decrease in life expectancy in Kohtla-Järve neighbourhoods

Discussion

The size of the health effect

The results of this analysis indicate that particulate air pollution is a significant public health issue in Estonia. In five main cities, the estimated annual number of premature deaths due to outdoor particles was 462, resulting in 6,034 YLL among 650,225 residents; this poses a considerable health concern. The decrease in life expectancy in the city centre of Tallinn can be as high as 1.17 years. Moreover, the effects of local heating can result in a decrease in life expectancy of approximately 1 year in neighbourhoods with dense small apartment buildings (Tartu, Pärnu). The daily average limit values of PM_{10} have been exceeded occasionally, resulting in an increased number of hospitalisations. When comparing our HIA results with those of other studies, our estimated average decrease of life expectancy of 0.63 years (7.6 months) is slightly lower than the 8.6 months arrived at for Europe (COMM 2005). Even if the assessment methods are somewhat different, from a PM standpoint, major Estonian cities are, on average, nearly as polluted as European urban areas. Calculated YLL from outdoor air pollution could contribute up to 5% of the burden of premature mortality in Estonia (Lai et al. 2009).

Air pollution induces illnesses, hospitalisations, and years of life lost, all of which have negative implications on a state's economy. The financial costs of health impairment are a tangible negative outcome that is acceptable to transitional societies where the socio-economic security is often prioritised at the expense of what has been called more "elusive" health concerns.

The societal costs of air pollution are relatively high. The estimates of the economic cost associated with health care because of air particulate pollution in Tallinn, Tartu, Kohtla-Järve, Narva, and Pärnu are, on average, €270 million. This corresponds to an estimate of approximately 3% of the cities GDP. Compared to the economic effect assessments for other European regions, the estimations in Estonia are relatively high. For example, in the EU assessment, the external costs of air pollution were estimated to correspond to slightly more than 1% of the GDP of EU (WHO 2005a). However, when the proportion is calculated from the cost estimation's upper confidence interval, the proportion is much higher (CI €79–190 billion). The assessment from more polluted regions, such as China, give estimations as high as 3.3% of the GDP (World Bank 2007). In extreme cases, such as Beijing, there have been even higher estimated costs, 6.6% of the GDP (Zhang et al. 2007). In Russia, it is as high as 6.5% of the GDP (Golub and Strukova 2008).

As mentioned above, the majority of the external costs from air pollution are related to premature deaths and not to hospitalisations and health care (ExternE 2005). However, there are many suggested effects typically not included in

the calculations, such as the induction of asthma and effects on children. The willingness to pay concept has been used in various calculations; these indicate the maximum amount a person would be willing to pay for an extra life year. It is a hypothetical variable, as health and well-being have no real market value. Moreover, respondents may consider it unethical to put a price tag on someone's death or illness (de Hollander and Melse 2006). Willingness-to-pay estimations are likely overstated. Therefore, it has been suggested that researchers should consider the external costs of the effect of air pollution on health as crude estimates, thereby allowing comparisons between different risks rather than regarding the expenses in real monetary terms (de Hollander and Melse 2006). However, we should not underestimate the value of external expenditure calculations as an instrument for analysing the costs and benefits of various environmental health policy options in specific socio-economic contexts.

Susceptible risk groups

Environmental health effects vary among different societal groups, and special attention should be paid to susceptible groups. There is a wide range of susceptibility within any large population, and certain individuals are at risk even at the lowest observed concentration levels (WHO 2006). This includes people with underlying health conditions, such as cardiovascular and lung diseases, asthmatics, socially deprived people, children, and the elderly. Due to a lack of data, some of the susceptible groups, such as children, are not very well described in impact calculations.

Our assessment in Tallinn revealed that even though the average loss of life expectancy in all citizens is 0.63 years, the loss per premature case is greater, with an estimation of approximately 13 years. This indicates that there are much larger effects among risk groups. As life expectancy and healthy-lived years are lower in Estonia than in the EU15 countries, the susceptible groups may be younger. However, the decrease in life expectancy in risk groups reported in our study is similar to Swedish results (Forsberg et al. 2005). When compared to Swedish cases, people in Estonia tend to die on average 6 years earlier, and the detrimental effects appear most in the younger age groups.

Modelled results

Dispersion models have not been widely used in studies on air pollution health effects. However, using modelled results, we can attain a more detailed picture of the exposure gradients in different parts of the city. A station represents a nearby neighbourhood or areas with similar characteristics. During the study period, air pollution was monitored at three sites in Tallinn, one site in Kohtla-Järve and at sites for short periods in Tartu, Narva and Pärnu. Air pollution dispersion modelling can also be used to construct scenarios of future trends and predict the extent of the health impact. The potential health impacts of air quality management programmes have been estimated prospectively (Mindell and Joffe 2004; Tonne et al. 2008; Tiwary et al. 2009).

However, there are several limitations to the disperson modelling methodology, the major one being the poor quality of the emissions data. To reduce the effect of this drawback, a database of local heating emissions was developed based on the results of a survey on fuel consumption (Kaasik et al. 2007). As the questionnaire was conducted several years ago in Tartu, and the results were then adjusted to reflect the conditions in four other towns, certain differences in results may exist (e.g. prevailing sources of pollution). The more frequent use of electric heaters and heat pumps may decrease the emissions from local heating, which may be the main reasons for the overestimation of emissions from local heating in Tartu and Pärnu. The considerable difference (on average 22%) between all monitoring stations and modelled PM levels is an important concern in terms of the reliability of the results. Thus, we should be careful in applying the results to other scenarios. However, as the concentrations have in some places been overestimated and in other places underestimated, the inaccuracy may not be crucial.

Estimates of the emission factors for traffic pollution dispersion modelling were determined using CORINAIR (EAA 2007). As there are negligible differences in car usage and climate, the differences are predictable. The modelled PM concentrations in Tallinn showed a relatively good agreement with measured values in the residential area and areas close to busy streets; however there was a considerable underestimation in the industrial area (Orru et al. 2009c). Even though the data on pollutant emissions and meteorology are representative, more advanced models also take into account land use, topography, buildings (especially street canyon models) and atmospheric chemistry.

Exposure resolution for the home address improves as the resolution of the air pollution modelling grid increases. On the other hand, the results become more sensitive to small errors in position of the source and receptor (i.e. home). In addition, as the dispersion modelling resolution is increased, the need for more precise emission data also rises. However, in real life, people move and spend time in different environments (e.g. indoors), and particles are usually measured outdoors. Thus, the personal exposure assessment has sometimes been implemented. Since this assessment method is relatively expensive, usually only 30–130 people are monitored (Nerriere et al. 2005; Williams et al. 2008; Folino et al. 2009; Scapellato et al. 2009). Another conflict arises in methodology, as we have used

more detailed modelled exposure data, whereas in original the ACS study (from where E–R relationships were implemented), the data from nearby monitoring stations had been applied (Pope and Dockery 2006). The spatial analysis methods have recently been implemented as well (Krewski et al. 2009).

Selection of E–R relationships

One of the crucial issues in the HIA process is the selection of the E–R relationship, as has also been discussed by Hubbell et al. (2009). The main problem lies in the lack of consistent long-term PM exposure effect studies for PM in Europe. One future possible solution could be the use of estimates from the ESCAPE (European Study of Cohorts for Air Pollution Effects) study (Brunekreef 2008).

In our HIA, we used the relationships reported from the American Cancer Society (ACS) study. The sensitivity analysis was also made with an E–R relationship from the same study, but a different baseline mortality indicator was used. One question arose regarding whether we can carry over the E–R relationships from the U.S. to the Estonian context. The pollution sources in Estonia are different; for example, there is a larger proportion of local heating. Additionally, the measuring sites might be dissimilar since primarily urban background levels are controlled and monitored in USA relative to only urban areas in Europe. Considering that the ACS study is the biggest air pollution cohort study to date and that it includes over 100 metropolitan areas, the results should show an average E–R relationship for all kinds of areas with multiple sources (Pope et al. 2002). Support for this point of view is found in the study by Jerrett et al. (2005), which is an analysis of ACS participants from California, where traffic-induced particles explain a bigger proportion of gradients in the PM pollution and where E–R relationships are nearly threefold higher. Krewski et al. (2009) extended the analyses, showing various E–R relationships in different parts of the country. A recent study in Tartu, Estonia indicated that the E–R relationship could actually be much higher for traffic-induced particles (Orru et al. 2009a). Thus, when conducting health impact assessments, prevailing pollution sources should be considered.

The question related to higher toxicity and effects per PM mass may have arisen in the Kohtla-Järve industrial area, where specific toxic pollutants, such as phenols, are very common. Our HIA showed smaller effects there as the outdoor annual mass concentration of fine particles was used as a pollution indicator. Therefore, largely used $PM_{2.5}$ mass concentrations may not have been the best indicator in this case. Finding the E–R relationship for special areas and special sources remains one of the main research challenges in future studies. Moreover, the model underestimated the concentration of fine particles in these towns.

Conclusions

There is a substantial exposure to PM in Tallinn, Tartu, Kohtla-Järve, Narva and Pärnu that cause considerable health effects in the form of cardiopulmonary diseases. Biomass combustion (local heating) and traffic remain the most important contributing factors to air quality degradation and the resulting adverse health effects. However, the assessment of the importance of the problem is not a straightforward task. The sources and effects are manifold and vary among different societal groups.

Characterising the effects among neighbourhoods could provide the public with a much better perception of the effects in different parts of the city. However, increasing the resolution also evokes many questions on methodology, particularly as the main pollution sources in cities were different, yet the same E–R relationship was used, possibly resulting in some bias. These factors indicate that the results of the HIA should be considered carefully as much expectancy has been assumed, and the assessed local condition may be somewhat different from the study sites where the original estimations were drawn from.

Acknowledgements The studies were funded by the Estonian Ministry of Environment. We would like to thank the local governments of these cities for supportive co-operation. The air quality assessment methods were partially supported by Estonian Ministry of Education and Research, research themes SF0180060s09, SF0180038s08 and SF1090050s07.

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Maasikmets, M.; Kupri, H-L.; Teinemaa, E.; Vainumäe, K.; Arumäe, T.; Roots, O.; Kimmel, V. (2016). Emissions from burning municipal solid waste and wood in domestic heaters. Atmospheric Pollution Research, Volume 7, Issue 3, 438–446

Atmospheric Pollution Research 7 (2016) 438–446

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Atmospheric Pollution Research

journal homepage: http://www.journals.elsevier.com/locate/apr

Original article

Emissions from burning municipal solid waste and wood in domestic heaters

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ARTICLE INFO

Article history:
Received 30 July 2015
Received in revised form
22 October 2015
Accepted 26 October 2015
Available online 21 November 2015

Keywords:
MSW and wood combustion
Emissions of PMx
PCDD/F
PAH
HCB

ABSTRACT

Waste burning is globally important emission source of several toxic compounds. The objective of this study was to acquire emission factors (EF) for PCDD/Fs, HCBs, PAHs, PMx and for several gaseous pollutants from the residential combustion, where wood is burned with municipal solid waste (MSW). In addition to the wood, paper and cardboard waste, people also tend to burn MSW. As the burnable waste content in MSW has changed during the past years, it is important to assess the effect of this factor for air emissions nowadays and in the past. Therefore an attempt was made to derive EF for the past emissions. 18 experiments including samples of firewood and MSW were burned using Estonian most common old type masonry heater, measuring PMx, PCDD/F, HCB, PAH-s and gaseous pollutants.

Significant correlation was found between PCDD/F, HCl, HCB and CO and between HCl and HCB in all 18 experiments. In three experiments (years 1990, 1995, 2000), the mean levels of PCDD/F were higher than the legislative limit value for combustion of MSW in waste incineration plants. The mean PCDD/F concentrations during the experiments was 0.0833 (0.0116–0.1550 95% CI) ng I-TEQ Nm^{-3} 11% O_2. Since low chlorine levels in used fuel caused high emissions of PCDD/F and HCB, it indicates that the habit of burning these kinds of waste in residential heaters should be avoided.

We can conclude that RWC is significant source of PCDD/F, HCB and PAH. In general, EF measured within this study are in accordance with literature data. There was remarkable difference in EF between different years. EF of PCDD/F and HCB found confirm the trend of development of MSW collection system leading to an increasing usage of MSW recycling. Nevertheless, people's awareness about the negative impacts of waste burning in household heaters, should be raised.

1. Introduction

Burning waste, whether at individual residences, businesses, or dump sites, is a large source of air pollutants. However, waste burning is not included in many current emission inventories used for chemistry and climate modelling applications (Wiedinmyer et al., 2014). Trash burning can be an important organic aerosol source and there are only few studies available (Mohr et al., 2009). There is an estimation that emissions of PM_{10} from open burning of domestic waste in China is equivalent to 22% of China's total reported anthropogenic PM_{10} emissions (Wiedinmyer et al., 2014). Waste burning is one important source of aerosols, which has been largely overlooked. It is estimated, that around 40 percent of the world's waste is disposed in this reckless and toxic way (Wiedinmyer et al., 2014).

Incomplete combustion occurs often during domestic heating, wherein organic material in the presence of chlorine causes the formation of chlorinated organic by-products, such as polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and hexachlorobenzene (HCB) (Hedman et al., 2006). In general, considerable PCDD/F emission reduction has been achieved with

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Peer review under responsibility of Turkish National Committee for Air Pollution Research and Control.

http://dx.doi.org/10.1016/j.apr.2015.10.021

respect to the industrial emission sources, whereas emissions from non-industrial sources hardly decreased (Quaß et al., 2004). According to the European Emission Inventory, wood combustion is one of the most important air emission sources for dioxins (Quaß et al., 2000). Based on the analyses of PCDD/F and PCBs in oil shale and fly ash from oil shale fired power plants in Estonia (covering more than 90% from Estonian electricity needs), it was concluded, that the power plants are probably not the major sources of dioxins in Estonia (Roots, 2004; Roots et al., 2015). Residential wood combustion (RWC) in wood heaters and fireplaces is estimated to account for 78% of PAH, 53% of PCDD/F 70% of HCB and 50% of $PM_{2.5}$ emissions in Estonia in 2010 (EEIC, 2012).

Biomass combustion is a major global source of fine PM in the atmosphere with significant impacts on regional air quality, visibility, ecosystems, human health, and global climate (Hobbs et al., 1997). Fine particulates, especially fine particulates ($PM_{2.5}$ and smaller), are particularly risky to human health, causing various respiratory and cardiovascular diseases, even lung cancer (Delfino et al., 2005; Pope et al., 2002). Estonia's health impact assessment study showed, that fine PM in ambient air has shortened the life expectance up to 13 months, with the highest decrease in city centres or areas with extensive domestic heating (Orru et al., 2011). Additionally, polycyclic aromatic hydrocarbons (PAH-s) are emitted during the biomass combustion, that have been proposed to cause high toxicity (Fernandez et al., 2001).

There is, however, lack of information concerning the characterisation of emissions from small scale biomass combustion systems. According to the Estonian Construction Registry there are around 164,000 households (30% from the total households) using wood for heating purposes, whereby more than 80% of them exploit old type masonry heaters. In Estonia wood and wood chips account >90% of the fuel used for residential heating (TUT, 2008). According to the members of Estonian Chamber of Chimney Sweepers evaluation (Kupri, 2014), in addition to the wood, paper and cardboard waste, people also tend to burn Tetra Pak's®, sanitary napkins, diapers, various plastic packages, shoes, textile etc. It is difficult to assess the exact number of people who still practice burning MSW since such activities are done clandestinely (Kupri, 2015b). PMF analysis of Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Inc.) dataset showed that during the heating season, plastic burning aerosols can be identified in residential areas (Maasikmets et al., 2015). Presumable, some households burn MSW on their domestic fires either to reduce fuel costs or to avoid disposal fees (Watson, 2012). Nevertheless, the issue of burning waste remains an important topic to address. The available evidence indicates that waste combustion in domestic conditions can be a significant generator of dioxins and, particularly, of PAHs. These emissions should therefore be reduced and eliminated where possible (Watson, 2012).

In addition to health effects caused by emissions from the MSW burning in households, quality of country specific emission inventories depend on reliable activity and emission data. Therefore verified EFs are needed for the annual emission reporting to the 1979 Convention on Long-range Transboundary Air Pollution (LRTAP) and to estimate the compliance with the Persistent Organic Pollutants (POPs) Protocol. At the moment, Estonia is not in compliance with the referred protocol. The main reason for being in non-compliance is caused by the fact, that during the past years the biomass, as an energy source, has been favoured due the climate policy and this has led to higher PCDD/F, HCB, PAHs and PMx emissions from the wood combustion sector, e.g. small scale combustion. On the other hand, used EF for national emission reporting are based on EMEP/EEA air pollutant emission inventory guidebook (EEA, 2013), where the given EF are highly uncertain and may differ from Estonia's conditions. In-field measurements make a better database for inventory EF as they take into account a several important factors for the level of the pollutant emissions, which include the co-incineration of wastes, the complete system consisting of combustion unit, flue pipe and chimney, memory effects in the chimney and the habitual practice of the operators (Hübner et al., 2005). These factors should be considered when compiling the national emission inventories and therefore, it is crucial to have EF which are representing, in more accurate way, the real situation in Estonia.

The burnable waste content in MSW has changed during the past 15 year; nevertheless our study enables to assess the possible effect of this factor for air emissions nowadays and in the past. Therefore an attempt was made to derive EF for years 1990, 1995, 2000, 2005, 2010 and 2013 using the amount of MSW generated during those years. The most common heater type (batch fuelled old type masonry heater) was used for measuring emissions from the 18 experiments carried out in EERC stove laboratory.

2. Methods and materials

According to Statistics Estonia, between 2000 and 2005, organized MSW collection systems covered 79% of the Estonia's population. By 2010 the percentage increased to 90% and by 2012 95% of Estonia's population was connected with the organized waste collection system (Statistics Estonia, 2015). MSW is an extremely heterogeneous material and the composition varies greatly between countries and even seasons (Lundin et al., 2013). For estimating the MSW generated, sorting studies of 2002 (Oras, 2002), 2007/2008 (SEI, 2008) and 2012/2013 (SEI, 2013) were taken into account for precise preparing the MSW content for the experiments. MSW burning experiments are based on the amount of MSW generated by Estonia's average household. Estonian average households are relatively small—according to Estonia's Statistics information in 2011, the average size of households consisted of 2.13 people (Statistics Estonia, 2014). For calculating the amount of MSW burned per household, a family of three as an average is taken into account in any observed year. It can be assumed, that people tend to burn flammable materials consisting plastic, paper and cardboard, wood, other flammable wastes and textile. Burning biodegradable waste is not included to this study, because biological treatment of solid waste is practiced widely. For determining year's specific EFs, MSW from Table 1 was burned together with firewood. More detailed overview about the content of MSW included to the experiments is described by Kupri (2015a).

Six experiments with three tests for each year (1990, 1995, 2000, 2005, 2010 and 2013) were prepared using firewood (alder, Alnus incana) mixed with common MSW in a way that different types of materials within the combustible waste material group were present. In each case, the wood was cut into pieces of 0.4–0.5 m length and split into halves or quarters. The wood was stored in a conventional way in an outdoor woodshed and was brought to heater laboratory at least 1 day prior to combustion experiment. The wood moisture content ranged between 14 and 18% on wet basis. The fuel net calorific value measured in all 18 experiments was 20.399 ± 0.662 MJ kg^{-1}. Analysis showed that the average chlorine content of the mixed fuel was 0.101 ± 0.034%. Fuel was ignited from the bottom, as this is the most common method used by the most of the heater users in Estonia. MSW was sourced from the Estonian Environmental Research Centre's kitchen, different households and a package waste receptacle of an apartment building.

Statistical variation between the data was analyzed by statistical software SPSS Statistics 17.0 (IBM SPSS Statistics), using Bivariate Correlation procedure to calculate Spearman Correlation Coefficient (Spearman's rho ρ, nonparametric correlations algorithm). Additionally descriptive statistics like mean, standard deviation

Table 1
Amount of MSW burned in households (kg) in different years.

Fuel type/Year	1990	1995	2000	2005	2010	2013
1. Plastic waste (kg)	0.147	0.217	0.245	0.175	0.104	0.108
2. Paper and Cardboard waste (kg)	0.153	0.227	0.257	0.164	0.078	0.081
3. Wood waste (kg)	n.a.	n.a.	n.a.	0.004	0.012	0.012
4. Other flammable materials (kg)	n.a.	n.a.	n.a.	0.060	0.073	0.075
5. Textile waste (kg)	0.020	0.030	0.033	0.042	0.029	0.031
Kg per household per day (three people)	0.959	1.4222	1.606	1.333	0.888	0.921
Hardwood (Alnus incana) (kg)	4.09 ± 0.03	3.55 ± 0.04	4.52 ± 0.20	3.67 ± 0.05	4.29 ± 0.13	4.25 ± 0.10

n.a. — not analyzed.

(SD) and 95% confidence interval (95% Cl) was calculated. In addition, principal component analysis (PCA) was used to evaluate similarities and dissimilarities between measured data. PCA is described as powerful multivariate data analysis technique in similar studies by many authors (Colombo et al., 2009; Hedman et al., 2006; Wikström and Marklund, 2001). The primary intention of PCA is to obtain an overview of the dominant "pattern" in a dataset (Wikström and Marklund, 2001). The obtained data was divided into different years (six experiments with three tests for years 1990, 1995, 2000, 2005, 2010 and 2013) and measured variables (concentration of measured gases, PMx, 17 PCDD/F congeners and 16 PAH compounds). The variables are used to characterize results from different years. PCA results are visualized using component plot in rotated space.

2.1. Emission measurements

18 samples of firewood and MSW were burned under laboratory conditions at the Estonian Environmental Research Centre's stove laboratory measuring PMx, PCDD/F, HCB, PAH and gaseous pollutants. All samples were taken from the hot flue gas from an Estonian old type masonry heater that was chosen for conducting the experiments, as more than 80% of households are using an old type masonry heater for heating purposes (TUT, 2008). The primary air access can be regulated manually with the heater door. Estonian old type masonry heater is in general similar to Finnish masonry heater, described by Tissari et al. (2009). The difference is that Estonian old type masonry heater does not have a secondary air access, therefore the combustion conditions may differ when comparing the results with the experiments made in the Finnish masonry heater. Similar to Finnish appliances (Tissari et al., 2009), also Estonian heaters are operated for a short time and at a high combustion rate, which is not always the case in Central-Europe, where mostly lightweight metal stoves are used and operated at the low combustion rate (Tissari et al., 2009). Based on assumptions given by many potters, during the experiments the heater door was open around 10% from the maximum, as this should represent habits used by the most of the population. As the draught in household chimneys is strongly influenced by the ambient conditions, flue gas blower on the top of chimney was used. Using flue gas blower it was possible to establish similar draught conditions (flue gas speed in chimney around 1.5–2 m s^{-1}) in all 18 experiments.

For the PCDD/F, HCB and PAH sample collection EVA Dioxin Sampler 1.5 E-type (Metlab Miljö AB) was used. All samples were taken from the hot flue gas according to standard EN 1948-1, through an externally heated metal tube of 180 °C that is connected to chimney. Inside the heated metal tube is a glass tube that has a pipe shaped nozzle that is pointed towards the analyzed gas flow. After heated tube, hot flue gas flows to a heated chamber where a fibreglass pre-filter separates solid particles. After passing the filter, hot flue gas flows through a glass spiral cooler column into a column filled with adsorbent (XAD-2). XAD-2 column is capturing PCDD/F, HCB, PAH from cooled flue gas after what sampling gas is dried and sucked through gas measurement clock to specify the gas volume. The glass tube, pipe shapes nozzle and glass spiral cooler are washed with acetone and toluene before and after experiments. Liquid collected for analyzing residue dioxins. Collected sample consists of a fibreglass pre-filter, XAD-2 adsorbent column and pre and after wash from glass details. PCDD/F (17 PCDD/F-s), HCB and PAH (16 PAH-s) analysis was performed in ALS Laboratory Group laboratory in Czech Republic, using a HRGC-HRMS (high resolution gas chromatograph and -mass spectrometer). ALS Laboratory Group operates a fully documented quality management system accredited by UKAS to the ISO/IEC 17025 standard.

PMx concentrations were sampled using Dekati® Diluter (2 stage dilution, 64 times dilution), where the sampling line was heated up to 180 °C and the filtered dilution air provided by the compressor was heated up in first stage up to 180 °C. For the second dilution stage filtered dilution air with room temperature (around 20 °C) was provided. For the PMx measurement ELPI™ (Dekati®, 12 size classes in range of 0.04–10 μm) and ELPI+™ (Dekati®, 14 size classes in range of 0.006–10 μm) was used. ELPI™ and ELPI+™ has been used in many RWC studies and Tissari (2008) and Obaidullah et al. (2012) have described it as suitable measurement technique for this purpose.

Simultaneously gas samples (SO_2, NO_x, CO, CO_2, HCl, HF, CH_4, O_2 and 11 calibrated volatile organic compounds), temperature (°C), water content (%) was measured during the whole burning process using Fourier Transform Infrared (FTIR, Gasmet Technologies Ltd.) analyzer. Insulated, externally heated (180 °C) sample line is leading gas through filter units to FT-IR gas analyzer. Calcmet Analyzis Software is used together with Gasmet™ DX-4000 analyzers to collect FT-IR spectra of the sample gas and to analyze the concentration of gas components.

Measured concentration was normalized according to methods described by Tissari (2008) and Van Loo and Koppejan (2008). For the EF calculation following equation (Ministerial regulation no 99, 2004; Tissari, 2008) was used:

$$q_i = c_i \times \alpha \times 0.25 \times k, \text{mg MJ}^{-1} \quad (1)$$

where: c_i – concentration in dry flue gas, mg Nm^{-3}; α – excess air $\alpha \approx 20.9/(20.9 - O_2)$; 0.25 – the dry volume of the flue gas per energy unit formed in the combustion of dry fuel, Nm^3 MJ^{-1}. k – fuel moisture factor.

3. Results and discussion

We found significant correlations between measured PCDD/F and HCl ($\rho = 0.932$[1]); PCDD/F and HCB ($\rho = 0.973$[1]); HCl and HCB ($\rho = 0.961$[1]) concentrations. The PCDD/Fs formation in MSW combustion processes are mainly involved by chemically similar

[1] Correlation is significant at the 0.01 level (2-tailed).

precursors, such as chlorophenols, which may be formed initially as the products of incomplete combustion (Altwicker and Milligan, 1993). PCDD/Fs may be produced from the reaction of volatile organic compounds (VOCs) and molecular chlorine under relatively low combustion temperature conditions (Liu et al., 2000). The small organic molecules can be adsorbed onto the fly ash from flue gases and are subsequently converted to PCDD/Fs. Compared with Cl_2, HCl is very unlikely to undergo aromatic substitution reactions to yield PCDD and PCDF precursors (Liu et al., 2000; Raghunathan and Gullett, 1996). Therefore, the formation of molecular chlorine may play a controlling role in the production of PCDD/Fs (Liu et al., 2000). Combustion experiments conducted in domestic stove burning hard coal demonstrated, together with a pronounced effect of the flue gas temperature, a predominant influence of the coal chlorine content on the PCDD/F emissions (Paradiz et al., 2015). On the other hand, Wikström and Marklund (2001) found, that the most important variable for changes in the PCDDs/Fs formation is disturbance in the combustion condition and not the variation in chlorine content of the fuel. Halász (1996) has found, that the PCCD/F emissions in stack gases depend strongly on the particle concentration. There are two temperature windows in which dioxin-like compounds can form: the "homogeneous" route between 500 and 800 °C and the "heterogeneous" one at 200–400 °C (Stanmore, 2004). When suitably catalyzed, PCDD/Fs also form on solid surfaces at temperatures of 200–400 °C. They can form via two routes, either from precursors such as chlorophenols and chlorobenzenes or from elemental carbon (the de novo reaction) (Addink and Olie, 1995; Stanmore, 2004). The heterogeneous route is probably dominating in RWC, as the temperatures in stoves used in RWC sector, are normally below 500 °C and high EC/OC concentrations in flue gases are normally observed (Tissari, 2008). Stanmore (2004) detected a good correlation between PCDD/F and other chlorinated products (and thus possible precursors). The maximum formation of PCDD/F occurred at 340 °C with the longest residence time (2.9 s) (Fangmark et al., 1994). In our experiments, similar temperature range and flue gas residence time was observed.

According to Hedman et al. (2006), HCB levels generally correlated with the PCDD/F levels. Nevertheless, the proportions appeared to be lower in the combustions with the highest PCDD/F levels, such as the intermittent pellet combustion and plastic waste combustion. This is indicating that conditions in these combustions may have specifically favoured dioxin formation rather than general POP formation. There were considerable differences between the EF in different years. Highest PCDD/F and HCB EF were measured with the fuel mix from the year 2000. This is probably caused by the fact that during that experiment biggest portion of MSW (1.606 kg) was burned with firewood. At the same time high CO, NO_x and PMx concentrations were measured, which indicates, that the combustion was due the small combustion chamber and high load of MSW, insufficient. Similar results were obtained also by Hübner et al. (2005). A positive correlation ($\rho = 0.829^1$) between PCDDs/Fs formation and CO concentration was found, which is in line with finding by Wikström and Marklund (2001).

Within our experiments, it was noticed that particulate number (PN) and HCl, CO_2 concentrations rose during the fuel adding process and CH_4 level rose during the mixing of fuels (see the Supporting Material, SM, Fig. S1). After adding fuel, CH_4 concentrations decreased, including a slight decrease in chamber temperature. CH_4 emissions are a result of too low combustion temperatures, too short residence times or lack of available O_2 (Van Loo and Koppejan, 2008). It was also observed, that during firing phase and after fuel adding PM size distribution changed slightly to bigger size fraction (SM, Fig. S2). Similar tendency was also observed by Tissari et al. (2009), where they noticed that the size distributions were widest during the firing phase when the sizes of the particles were also larger. This is probably caused by insufficient supply of air and insufficient mixing of air and fuel. HCl concentrations increased rapidly after adding fuel and stayed high for few minutes, after what, the concentrations decreased until new fuel was added. This phenomenon was more clearly evident at the beginning of test, shown in SM Fig. S1, as chloride compounds are due the high vapour pressure volatile. HCl concentrations formed during fuel combustion are usually related to the chlorine concentration of the burned fuel. In all fuel adding similar fuel mix was used, nevertheless, MSW content may vary from batch to batch, as all MSW batches were composed manually. For more homogenous fuel mix shredded MSW could be used, but in our experiments this was avoided, as this doesn't represent the situation how the MSW is burned by people in households. In our experiments, chamber temperature increased rapidly up to 300 °C at the beginning and approximately after 1 h reached maximum around 400–500 °C. After reaching temperature around 400 °C, HCl concentrations slowly dropped down. Fuel mixing did not increase HCl concentrations. According to Miller et al. (2003) the chlorine in the fuel has been found to play an important role in the release of ash-forming elements to gas phase. The metallic chlorides, in biomass combustion typically alkali metal chlorides, have high vapour pressures and hence, they condense at low temperatures in the flue gas. The behaviour of chlorine is strongly affected by fuel sulphur content (Sippula, 2010). On the other hand, the fuel sulphur has been seen to affect the particle formation in several ways. Throughout the sulphation reaction, chlorine of the metallic chloride is released as HCl (Sippula et al., 2008). Additionally Sippula et al. (2008) has found, that the increase of HCl in the combustion increased both PN concentration and mean particle size and obviously, the fine particle mass concentration. Similar tendency was also observed during our experiments (SM Fig. S1).

PAH (Fig. 2) has the highest EF during 1990 year experiment, which is not following the overall trend regarding other EF, where the highest EF were observed with mixtures including highest MSW load. Nevertheless, also during 1990 year experiment the MSW load was high, which has probably led to the high EF.

EF of PMx and gases are following similar trend with PCDD/F and HCB EF, where the highest EF (except SO_2) were measured during the year 2000 experiment, where the fuel load (incl. highest MSW load) was highest and therefore the optimal combustion conditions were not achieved. Highest SO_2 EF was measured during the 2010 year experiment, which was caused by higher sulphur content (0.14%) of fuel.

Mean PCDD/F concentrations were in range within 95% CI of 0.0116–0.1550 ng I-TEQ Nm^{-3} 11% O_2. The highest PCDD/F level was found in the year 2000 samples and highest levels of 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF were identified (SM Fig. S3). No PCDD compounds were found from the samples. This finding is in line with the statement reported previously that the PCDD/Fs formed in wood combustion are mainly PCDF compounds (Kaivosoja et al., 2012; Tame et al., 2009). In three experiments (years 1990, 1995, 2000) the mean levels of PCDD/F were higher than the legislative limit value for combustion of MSW in waste incineration plants, which is for PCDD/F 0.1 ng I-TEQ Nm^{-3} (11% O_2) (IED, 2010). Mean PCDD/F concentrations measured during the experiments, are generally in the same range of limit value set for the MSW incineration plants. Similar results were obtained by Schatowitz et al. (1993), Fiedler (1993), Launhardt et al. (1998), Pfeiffer et al. (2000) and Wevers et al. (2004). As quite low levels of chlorine caused this effect, it indicates, that the habit of burning these kinds of waste in residential stoves should be avoided.

Our results for the concentration of NO and NO_2, in comparison with Hedman et al. (2006) experiments 2.4a and 2.4b, where

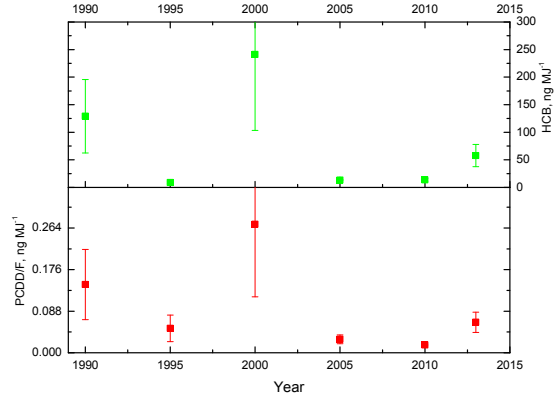

Fig. 1. PCDD/F and HCB EF with standard deviation.

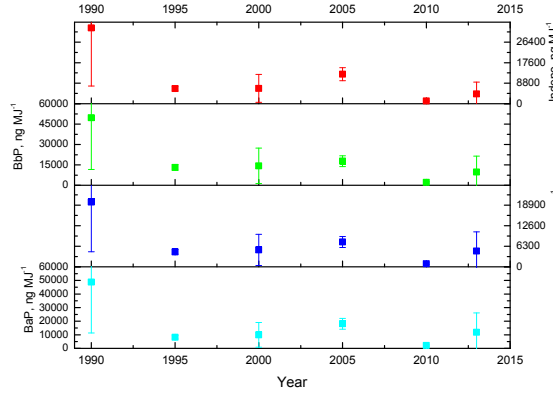

Fig. 2. BaP, BkF, BbP and Indeno (1 2 3-cd)pyrene EF with standard deviation.

birchwood was burned with paper and plastic, were slightly higher and for all other compounds lower (Table 2). The biggest difference is in PCDD/F results, as our measurements showed on average 145 times lower results. Taking into account, that results by Hedman et al. (2006) are expressed in WHO-TEQ and they are on average 10–20% higher compared to I-TEQ values, than our results remain still much lower. Also the SO_2 concentration from Hedman et al. (2006) exp. 2.4b is around 51 times higher compared to ours.

Table 2
Comparison of measured data.

Substance (273.15 K, 101,325 kPa, 10% CO_2)	This study, mean	Hedman et al. (2006) exp. 2.4a	Hedman et al. (2006) exp. 2.4b
CO, g Nm^{-3}	4.64	7.6	26
NO, mg Nm^{-3}	167.73	130	40
NO_2, mg Nm^{-3}	218.47	31	130
SO_2, mg Nm^{-3}	32.99	0.1	1700
HCl, mg Nm^{-3}	16.70	44	130
PCDD/F, pg Nm^{-3}	106.45 (I-TEQ)	$6.9 \times 10^3 \pm 690$ (WHO-TEQ)	$24 \times 10^3 \pm 1.4 \times 10^3$ (WHO-TEQ)

This indicates that at least during the exp. 2.4b, quite high sulphur containing fuel was used. Nevertheless, in Hedman et al. (2006) exp. 2.4b even higher PCDD/F results were obtained compared to exp. 2.4a, where the fuel SO_2 concentration was 0.1 mg Nm^{-3} (at 273.15 K, 101,325 kPa, 10% CO_2). This is in contradiction with findings by Liu et al. (2000) and Addink et al. (1996), where high sulphur content in fuel was found as good inhibitor for PCDD/F formation. The main reason for having differences in PCDD/F results compared to Hedman et al. (2006) can be that different type and amount of MSW was used and in our case, the experiments were done using masonry heater, while Hedman et al. (2006) in experiments 2.4a and 2.4b has used an approximately 30-year old boiler. For PCDD/F formation (heterogeneous reaction) gas residence time in order of second in combustion chamber for certain temperature range (200–400 °C) is needed, in our case this criteria is fulfilled. Furthermore, as the flue gas moves inside the heater are around 5000 mm long (additionally to flue gas residence time 2–3 s inside the heater), after that the flue gas is cooled down around 2 times. In sampling point the normal temperature stays around 100–200 °C, which is 2–4 times lower compared to temperatures in combustion chamber. Such conditions in conjunction with chlorine have been found suitable for PCDD/F formation (Wikström et al., 2003).

The mean PM_{10} concentration during the experiments was 1113.55 (275.2–1951.9 95% CI) mg Nm^{-3} (13% O_2). Highest concentrations were measured during year 2000 experiments, with the mean level of 2384.461 (618.083–4150.840 95% CI) mg Nm^{-3} (13% O_2). High concentrations were caused by high load of MSW and concentrations rose during the fuel adding significantly. In average, during year 2000 experiment, mean concentration of CO was 3847.11 (2271.88–5422.34 95% CI) mg Nm^{-3} (13% O_2). PM emission and size distribution from heaters largely depends on combustion conditions (SM Fig. S1), which is mainly caused by incomplete combustion due to too fast pyrolysis and increased ash release due to high combustion temperature. We noticed remarkable increase of PM and PN concentrations during the firing phase and fuel adding, in line with findings by Tissari et al. (2009).

Comparing POP EF from MSW combustion only few literature reports on emissions from masonry batch fuelled heater, where the wood is combusted with MSW, were found. In a series of field studies of domestic heating appliances Hübner et al. (2005) found highest PCDD/F emissions (0.03–0.1 ng I-TEQ MJ^{-1}) when relevant amounts of other combustible materials, such as MSW, were co-combusted or used in order to facilitate lightning-up. In average, EF for PCDD/F (Table 3) measured within this study are lower compared to Hübner et al. (2005), nevertheless, results from year 2000 experiments (Fig. 1) (highest MSW load) are in the same range (0.0050–0.5392 95% CI ng I-TEQ MJ^{-1}). According to EEA (2013), EF for conventional stoves using wood and similar wood waste are within 95% confidence interval (95% CI), in range from 0.02 to 5 ng I-TEQ MJ^{-1}.

In average, the EF for HCB concentration found within this study are in range of 10.744–143.817 ng MJ^{-1} (95% CI), which is much higher compared to default EF from EEA (2013), where the EF 5 ng MJ^{-1} for conventional stoves using wood and similar wood waste is proposed. According to EEA (2013), emissions of HCB from combustion processes are highly uncertain, but on the whole, processes resulting in PCDD/F formation is also leading to HCB emissions. Similar to high PCDD/F emissions, highest HCB emissions were measured during the year 2000 experiments, where we obtained mean EF of 241.216 (4.447–477.985 95% CI) ng MJ^{-1}.

Mean PAH concentration (16 PAH) was in range within 95% CI of 0.451–5.774 mg Nm^{-3} (13% O_2). PAH profiles varied between the different samples. Naphthalene, acenaphtylene, fluorine and phenanthrene were among the four most common PAH compounds (SM Fig. S4) during the tests and contributed from 80% to 95% of the total PAHs. Similar results were obtained also by Kaivosoja et al. (2012). EF for PAH-s (benzo(a)pyrene, benzo(k)fluoranthene, benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene) are much higher compared to results proposed in EEA (2013), where EF within 95% CI were for benzo(a)pyrene is in range of 12–1210 ng MJ^{-1}, for benzo(k)fluoranthene 4–420 ng MJ^{-1}, for benzo(b)fluoranthene 11–1110 ng MJ^{-1} and for Indeno(1,2,3-cd) pyrene 7–710 ng MJ^{-1}. The emission of PAH depends mostly on the combustion process, particularly on the temperature (lower temperatures favourably increases their emission), residence time in the reaction zone and the availability of oxygen (EEA, 2013; Van Loo and Koppejan, 2008). The main reason for high level of PAH, is due to the low temperatures in combustion chamber during the firing and high fuel load. In our experiments, we added MSW to wood, which may lead to poor combustion conditions in the heater chamber.

PCA was used to evaluate the potential variation and similarities of the measured variables, consisting of 18 emission test and 41 variables (17 PCDD/Fs congener patterns, 16 PAH compounds and other measured variables) in flue gas samples. Fig. 3 is showing a distinct correlation between the formation of the variables. Based on the two components extracted from PCA, the first principal component (Component 1) accounted for 84.1% of the total variance, and the second principal component (Component 2) accounted for 15.2% of the total variance. The score plot (Fig. 3) of PCA indicated that all the measured variables can be assigned to four groups. Group 1 includes only SO_2, which can be explained by the fact that mostly more than 95% of SO_2 is result of complete oxidation of the fuel sulphur. Group 2 includes several compounds, like all PAH-s, particulates, CO, CH_4, VOC and N_2O. This group consists mainly compounds (except N_2O), which are result of incomplete combustion. Group 3 includes CO_2 and NO_x, which are results of complete combustion. Group 4 includes mainly chlorinated compounds, including all PCDD/F-s, HCB and HCl. This indicates that HCl and PCDD/F, HCB are strongly correlated and we can assume that within our tests fuel chlorine content played important role in PCDD/F and HCB formation.

Nonparametric statistics was used to test the correlation of measured variables in Group 2, Group 3 and Group 4 (Group 1 was not included due to only one variable). Spearman's rank correlation coefficient matrix of Group 2, 3 and 4 showed strong correlation between some variables, especially in Group 4. The correlation coefficients of 4 are all (except HF) higher than 0.8 and are significant at the 0.01 level. Some results of nonparametric statistics verified well with the PCA. For the proper PCA analysis more results are needed and therefore PCA analysis with only 18 results may be insufficient.

4. Conclusions

Significant correlation between measured PCDD/F and HCl ($\rho = 0.932^{1}$); PCDD/F and HCB ($\rho = 0.973^{1}$); HCl and HCB ($\rho = 0.961^{1}$); PCDDs/F and CO ($\rho = 0.829^{1}$) concentrations was found. In three experiments (years 1990, 1995, 2000) the mean levels of PCDD/F, was higher than the legislative limit value for combustion of MSW in waste incineration plants. Quite a low levels of chlorine in used fuel resulted with rather high emissions of PCDD/F and HCB. This is indicating that the habit of burning these kinds of waste in residential heaters should be avoided.

PCA was used to evaluate the potential variation and similarities of the measured variables. The score plot of PCA indicated that all the measured variables can be assigned to four groups. Group 4 includes all PCDD/F-s, HCB and HCl with all the compounds

Table 3
Mean EF (95% CI of mean)

Substance, unit	EF, mean	Lower 95% CI of mean	Upper 95% CI of mean
PCDD/F, ng MJ^{-1}	0.059	0.020	0.098
HCB, ng MJ^{-1}	48.469	13.299	83.638
Benzo(a)pyrene, ng MJ^{-1}	16502.425	6023.862	26980.988
Benzo(k)fluoranthene, ng MJ^{-1}	7172.284	2939.232	11405.337
Benzo(b)fluoranthene, ng MJ^{-1}	17764.485	7229.314	28299.656
Indeno[1,2,3-cd]pyrene, ng MJ^{-1}	10599.901	3648.999	17550.803
PM_1, mg MJ^{-1}	975.960	103.140	1848.780
$PM_{2.5}$, mg MJ^{-1}	1027.327	108.569	1946.084
PM_{10}, mg MJ^{-1}	1048.292	110.785	1985.800
CO, mg MJ^{-1}	2839.242	2154.374	3524.109
N_2O, mg MJ^{-1}	1.782	1.180	2.385
NO_x, mg MJ^{-1}	469.528	370.175	568.881
SO_2, mg MJ^{-1}	19.988	11.988	27.988
NH_3, mg MJ^{-1}	3.460	0.297	6.623
HCl, mg MJ^{-1}	9.242	2.181	16.302
HF, mg MJ^{-1}	1.568	0.813	2.323
VOC, mg MJ^{-1}	645.395	491.489	799.301

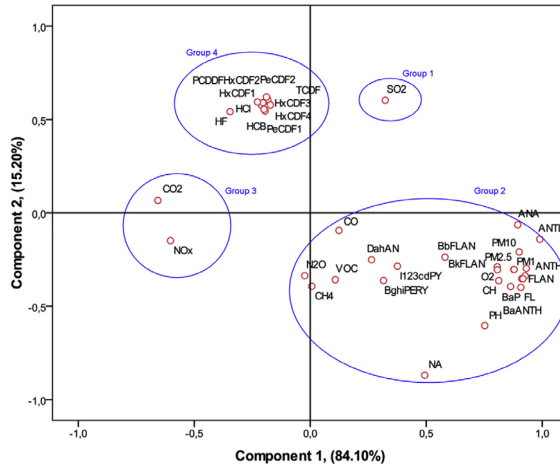

Fig. 3. Principal components plot of the measured concentrations (acronyms names are given in SM Table S1).

strongly in correlation, therefore we can assume that within our tests, fuel chlorine content played important role in PCDD/F formation.

From our experiments we can conclude, that there was remarkable difference in EF between different years. PCDD/F and HCB EF conform to the development of the MSW collection system in Estonia (since 2005, parishes with more than 1500 inhabitants are obligated to join to the organized waste disposal system). Development of the waste disposal system has led to an increasing trend of waste recycling, instead of burning it either in heaters or in backyard. As nowadays more plastic waste is recycled, it can be assumed that less plastic waste is burned in household heaters as well. Nevertheless, there are still households which are practicing such kind of activity; therefore people's awareness about the negative impacts (environmental and technical regarding heater maintenance) of waste burning in household heaters should be raised.

We can conclude that EF obtained during experiments can be used in national emission inventories, as they are representing local circumstances regarding MSW burning in household heaters. We can conclude that RWC is significant source of PCDD/F, HCB and PAH, as RWC is estimated to account for more than 50% of PCDD/F, more than 70% of HCB and more than 80% of PAH emissions in Estonia in 2013.

Nowadays more masonry heaters with secondary air excess are built, which are similar to Finnish masonry heaters described by Tissari et al. (2009), therefore further studies are needed to investigate emissions from those heater types, including local habits of fuel usage and operational circumstances. Further research is also

needed to validate the obtained EF, combining dispersion calculations and ambient air measurements.

Conflict of interest

The authors declare no conflict of interests.

Acknowledgements

We would like to acknowledge to Estonia's Ministry of Environment for providing resources to M. Maasikmets, H.-L., Kupri, E. Teinemaa, T. Arumäe and K. Vainumäe with financing project no 4-1.1/14/189 and Estonia's Ministry of Education and Environmental Conservation and Environmental Technology R&D Programme for providing resources to V. Kimmel and M. Maasikmets correspondingly with targeted financing project SF1090050s07 and project BioAtmos (3.2.0802.11-0043).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apr.2015.10.021.

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III

Maasikmets, M.; Arumäe, T.; Teinemaa, E.; Kimmel, V. (Submitted). Development and preliminary assessment of a mobile non-exhaust emission measurement laboratory REAL. Submitted.

DEVELOPMENT OF A MOBILE NON-EXHAUST EMISSION MEASUREMENT LABORATORY REAL

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Abstract. Non-exhaust particulate matter (PMx) emissions from traffic are influencing the air quality and therefore it is important to develop measurement devices which are suitable determine the PMx emissions during actual driving conditions. The objective of this study was to develop a representative device for sampling and measurement of PMx emissions originating from tyre, brake pad and pavement wear in road transport. Besides developing the measurement device, another objective of the study was to test the suitability of the method and the measurement device. Test measurements were carried out to test the dependence of PMx emissions on various factors like vehicle speed, tyre and tyre type (studded, non-studded and summer tyres). The emission factor (EF) of PM_{10} for non-studded tyres measured with the REAL system was 32.64±5.28 mg vkm^{-1}, which is comparable to published data. Highest PM_{10} emissions were observed with studded tyres and at speeds above 50 km h^{-1}. Studded tyres produce a greater proportion of coarser particles when compared to non-studded and summer tyres, while the particle size with the highest mass concentration is around 8 µm for both the non-studded and studded tyres. We could not observe any formation of nanometer-size particles due to the tyre temperature increase and loosely bound tyre material evaporation. Nevertheless further research is still needed to investigate the nanometer-size particles formation from the tyre material. It can be concluded that the developed measurement system, REAL, is suitable for measurement of PMx emission originating from tyre, brake pad and pavement wear in road transport.

Keywords: resuspension, non-exhaust emissions, studded tyres, PMx, mobile measurements

1. Introduction

Fine particulates ($PM_{2.5}$ and smaller) are particularly risky to human health, causing various respiratory and cardiovascular diseases, even lung cancer (Delfino et al., 2005; Pope et al., 2002). In daily life, people are mostly exposed to fine particulates at work or in street traffic; therefore this study focuses on fine particulate releases from street traffic. Areas along the streets have higher fine particulate concentrations compared to urban backgrounds and mixed type areas (Saare et al., 2013).

Estimation of non-exhaust traffic emissions is important, as earlier studies have shown that fine particulate emissions from this sector have a significant effect on urban air quality (Bukowiecki et al., 2010). Studies in several European cities have shown that about half of total fine particulate emissions are made up of particulates originating from surface wear. In European countries that use traction sand, salting and studded tyres against skidding in winter, the PM_{10}

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* - working as a freelancer at the momnet

fraction originating from surface wear can reach 90%. (Forsberg, 2005; Omstedt et al., 2005). Non-exhaust vehicle emissions are formed from wear particles of vehicle components such as brakes, clutches, chassis and tires. Although the non-exhaust particles are relatively minor contributors to the overall ambient air particulate load, reliable exposure estimates are limited. (Panko et al., 2013). Suspended road dust will remain a problem because of an increasing number of vehicles in urban and rural areas. Only few real-world measurements of road dust resuspension have been performed to date. There is still a knowledge gap regarding the dominant mechanisms leading to road dust emissions, although resuspension of surface particle loading obviously plays an important role. (Pirjola et al., 2010). Measurements in Scandinavia show that the proportion of particulates originating from pavement is significantly higher in winter and early spring measurements (Hussein et al., 2008). This is believed to be the primarily caused by anti-skid treatments and studded tyres. The subject matter is important, as problems with particulates remain a vital issue in Estonia and elsewhere in Europe.
Road transport particulate emissions and non-exhaust emissions have previously mostly been studied using fixed roadside measurement equipment (Bukowiecki et al., 2010; Norman and Johansson, 2006) and in laboratory conditions (Dahl et al., 2006; Gustafsson et al., 2008). Laboratory test results are difficult to translate to actual traffic conditions, as they are obtained in controlled simulated conditions. Stationary devices measure background air and vehicle exhaust emissions in addition to particulates from road abrasion. Mobile measurement allows measurement of particulate emissions in actual traffic conditions using actual vehicles and loads. It also allows reducing the effects of possible confounders like exhaust gases, weather conditions (air movement, inversion) or areas with limited air movement. By using actual vehicles, it allows studying of the effect of different tyre types (summer, non-studded, studded) on formation of PMx.

2. Methods and materials

Measurement device design started with review of earlier studies (Hussein et al., 2008; Mathissen et al., 2012; Pirjola et al., 2009) based on the results and recommendations of these studies, a mobile measurement system was built that allowed measurement of fine and coarse particulates originating from road and tyre wear.
Using results from above mentioned other studies, a mobile measurement laboratory REAL (Road Emission Aerosol Laboratory) was built that is capable of measuring PMx originating from vehicle tyre, brake pad and road pavement abrasion. The sampling of PMx is done directly behind the both back wheels of the vehicle and the PMx background concentrations were measured in front of the vehicle. The REAL measurement system can also measure vehicle exhaust gases under field conditions.
To prevent entry of moisture and splashes into the measurement system where they would affect accumulation of particulates, the device can only be used in dry weather and on relatively dry road conditions. Other weather conditions, like wind velocity and temperature, have little effect on the measurement, as long as sampling is done at the centre of the tyre and not further than 10 cm from the tyre surface (Etyemezian et al., 2003).

Altogether 4 tests with studded and non-studded tyres were done in April 2013, at a time when use of winter tyres is still allowed in Estonia. Tests with summer tyres (5 altogether) were done in summer 2013 and 2015.

2.1. REAL technical specifications

Test were done with Toyota Hilux (2006) 2,5 TDI, (turbo diesel) with an 88 kW (118 hp) engine. Vehicle dimensions: length 5255 mm, width 1760 mm, height 1810 mm, authorized

weight 2760 kg. Load on rear axle, where the probe was located, was 1510 kg. Summer tyres used in testing were Michelin Latitude cross summer tyres, sized 265/70 R15. Studded tyres used were Cooper Discoverer 265/70 R15 M+S, non-studded tyres were Bridgestone Blizzak 265/70 R15 M+S. The vehicle was equipped with a modified trailer carrying analyzers and other necessary equipment. Trailer dimensions were: length 5140 mm, width 1920 mm, height 2334 mm, authorized weight 1700 kg. (Figure 1).

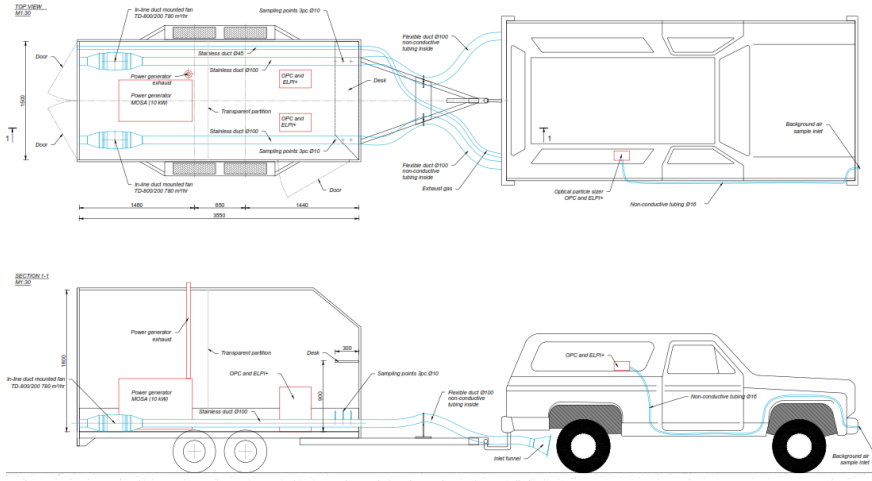

Figure 1. Schematic diagram of REAL

Figure 2. Positions of the temperature sensors and sampling inlet

During measurement, rear-wheel drive was used. The trailer housed particle analyzer Dekati ELPI+^{TM} (size range 6 nm – 10 µm, Electrical Low Pressure Impactor, Dekati Ltd), its pump, optical particle analyzer OPS (size range 300 nm - 10 µm, Optical Particle Sizer 3330, TSI Ltd), an air compressor for cleaning thermal sensors (GIS, SIL AIR 50/9, Silentaire Technology Ltd), and other equipment (electric generator, sampling probes with adjustable fans, controller computer, data loggers for thermal sensors, UPS, electrical switchboard).

Compact infrared temperature sensors (Optris CT LT, Optris GmbH) that measured tyre and road surface temperatures were attached to the footboard of the vehicle (Figure 2). These sensors determine the temperature of an object's surface using an infrared sensor. Tyre temperature sensor was positioned horizontally, so that it could be pointed directly at the tyre. Pavement temperature sensor was positioned vertically, so that it could be pointed directly at the pavement. Filtered compressed air was directed at both sensors at 1-2 l min^{-1} to keep them clean and prevent errors due to surrounding dust. Electricity for the analyzers and other equipment was produced by a diesel generator (GE 12000 LD/GS, MOSA, BCS Group) with a capacity of 10 kW. Diesel generator exhaust gas was directed out through the roof and thus did not affect measurement results. The vehicle was equipped with a GPS that could record vehicle coordinates (in degrees) and speed (in km h^{-1}) at 5-second intervals. A special sampling inlet, with a surface area of 400 cm^2 and a sieve with a pit diameter of 3 mm preventing entry of large particles, was installed in the vehicle's wheel arch (2). 2 sampling probes with a diameter of 100 mm and length of 3000 mm (non-conductive tubing inside a flexible probe between the vehicle and the trailer) + 3563 mm (a probe in the trailer fixed horizontally to the floor of the trailer). Air exited via openings in the rear doors of the trailer. Both sampling probes had three 10 mm diameter vertical sampling points that provided sampled air to the analyzers. An ELPI+ thermal sensor was fitted in the sampling probe for measuring the temperature of the analysed

air. The trailer also contained a 50 mm diameter probe for vehicle exhaust gas that was vented to the back of the trailer and routed the vehicle exhaust gas away from sampling point. The setup also allows vehicle exhaust gas measurements under actual driving conditions. To allow isokinetic sampling, the sampling probes were fitted with adjustable suction fans at the end (TD-800/200, max suction 2x1100 m^3 h^{-1}). Air speed inside probes was spot-checked via pressure difference using a Testo 400 automated analyzer (Testo AG, GmbH). To ensure constant isokinetic sampling, a stationary anemometer should be fitted inside the measurement probe and fan speed adjusted according to anemometer reading.
To measure background air, a non-conductive sampling probe was fitted to the front bumper of the vehicle; from where the background air was sampled by an OPS and ELPI+.
Optric CT LT compact infrared temperature sensors were used to measure tyre and road surface temperatures. These are infrared sensors capable of measuring the temperature of a surface with up to a millisecond resolution. In these tests, tyre and road surface temperatures were measured at 1 second intervals. As dust would inevitably be collected on sensor lenses during measurement, filtered compressed air is constantly blown over the lens surface at a low speed of 1-2 l min^{-1} using a compressor in the trailer. This creates an air cushion that prevents dust deposition on the lens and consequent effects on temperature reading (OPTRIS, 2013).

2.2. Emission measurements

Test measurements for REAL logged data about tyre and road surface temperature, background air particulates concentration, vehicle location and speed, and PMx emission from tyre, brake pad and road pavement abrasion. Background concentrations of PMx and concentration peaks caused by passing vehicles or roadside sources (dust-producing farming activities, unpaved side roads etc.) were subtracted from the results.

Additional tests were carried out to evaluate sampling losses of PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ in sampling system. For this, parallel measurements were done with two OPS and ELPI+ devices. For this, the probe of one OPS and ELPI+ analyzer was placed immediately in front of the sampling inlet behind rear wheel, and the other OPS and ELPI+ analyzer measured from the measurement system's regular sampling location. The test showed that the loss of PM_{10} fraction in the measurement system's probe was around 46 %, for $PM_{2.5}$ and $PM_{1.0}$ fraction 13.5% and 2.4% respectively. Those losses were taken into account when EFs were calculated. In the future, new measurements could be done to evaluate losses of different fine particulate fractions using an aerosol generator. In such a method fine particles of known size and concentration are generated, injected into sampling probe, and fine particulates sampled using the sampling system. Such a method can efficiently assess losses of different fine particulate fractions in the sampling probe.
The suitability of REAL for the stated purposes was evaluated in test measurements. Test measurements evaluated the effect of different tyre types and vehicle speed on PMx emissions generated. Using measured concentrations, emission rates (milligrams per second, mg s^{-1}) and EF (milligrams per kilometre of travel, mg vkm^{-1}) can be calculated for a specified pollutant. EF was calculated using the following equations (Mathissen et al., 2012):

$$E = \sum_t c_{av} \cdot A \cdot v_{vehicle} \qquad \textbf{Equation 1}$$

$$EF = \frac{E_{Total}}{d} \pm \frac{Stdev}{d} \qquad \textbf{Equation 2}$$

where:

E is the emission rate (mg s^{-1});
EF is the emission factor (mg vkm^{-1});
Cav is the averaged background corrected PM10 mass concentration (mg m^{-3});
A is the surface area under the wheel (0.1 m^2);
vvehicle the velocity of the vehicle (m s^{-1});
d is the distance travelled;
Stdev is the standard deviation of the emission rate.

3. Results and discussion

Results (Figure 3) show that the PM_{10} EF is the greatest with studded tyres, at speeds both below and above 50 km h^{-1}. This is predominantly caused by greater abrasion of road surface by studded tyres, and the studs' own wear in this process. High EF of non-studded tyres is primarily caused by their softer material compared to summer tyres and resulting greater wear. The proportion of PMx originating from worn rubber in the samples can be assessed by later analysis of filters. At this time of the year there is also a significant PM contribution from particles resuspended by vehicles from road surface, as the roads are covered by significant amounts of material deposited there by traffic and other sources during winter and spring. In winter, abraded pavement material usually sticks to the surface due to moisture, and freezing then binds particles to the road surface. With rising temperatures, previously deposited and frozen particles are freed from the surface and hurled into the air by tyres. Summer tyre material is harder and road surface generally cleaner in summer.

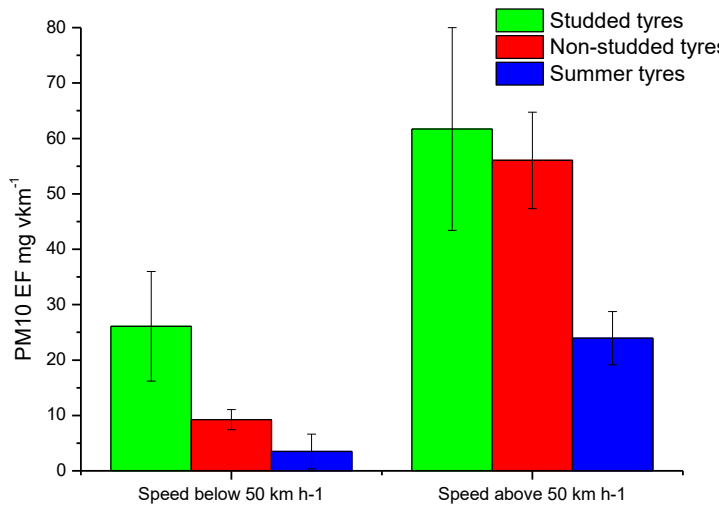

Figure 3. PM_{10} EF dependency from vehicle speed and tyre type

Somewhat higher EF of non-studded tyres, when compared to summer tyres, is caused by their softer material and deeper treads that create a stronger vacuum when contacting pavement, and resulting greater amount of fine particulates thrown into the air.

The mean PM_{10} EF of non-studded tyres was 32.64±5.28 mg vkm^{-1}, which is comparable to published data of 26 ± 19 mg vkm^{-1} (Mathissen et al., 2012) and 30 ± 14 mg vkm^{-1} (Bukowiecki et al., 2010).
Figure 4 shows the relationship between PM_{10} mass concentration and vehicle speed in summer tyre test. This trend is confirmed by earlier studies (Mathissen et al., 2012; Pirjola et al., 2009). Particles in 1 – 8 µm range are produced most abundantly (Figure 4). Higher emission of fine particulates at higher speeds is caused by the stronger forces acting between the tyre and the road surface; these produce more wear on both the pavement and the tyre. Higher speed also causes more air turbulence under the vehicle, this lifts more particles off the surface.

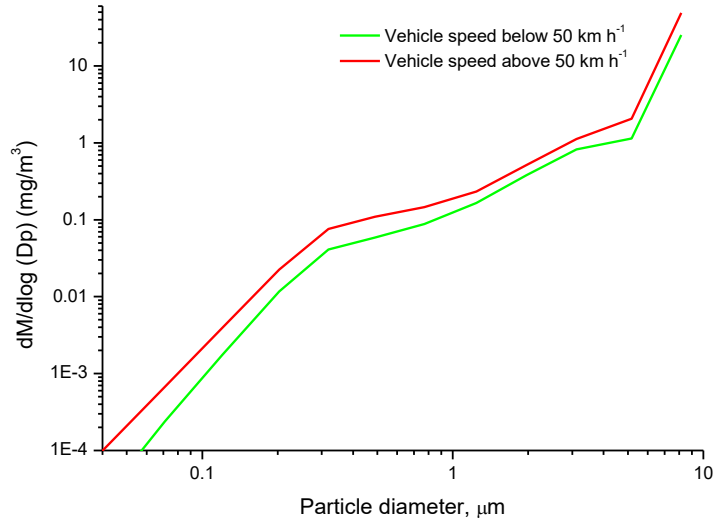

Figure 4. PMx mass concentration (mg/m^3), size distribution and their dependency from the vehicle speed

The largest mass concentration of particles is produced in the coarser particle size fraction, varying somewhat depending on tyre type. Studded tyres produce a somewhat greater proportion of coarser (0.5 to 8 µm) particles when compared to non-studded and summer tyres, while the particle size with the highest mass concentration is around 8 µm for both the non-studded and studded tyres (Figure 5). More varied fraction distribution of studded tyres when compared to non-studded and summer tyres might be explained by differences between studs.

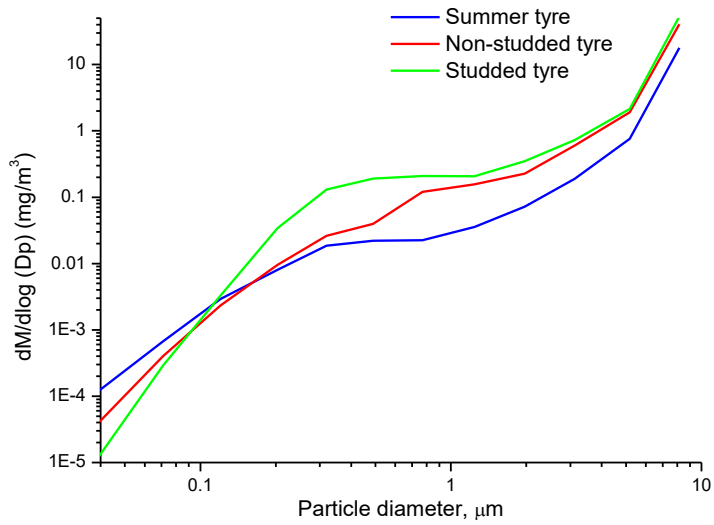

Figure 5. PMx mass concentration (mg/m^3), size distribution and their dependency from used tyres

Preliminary testing confirmed the suitability of REAL for the measurement of PMx emission originating from vehicle tyre, brake pad and road pavement abrasion. REAL has the advantages of compatibility with different vehicles and of an autonomous electrical power that allows the use of different measurement devices. While measuring PMx originating from pavement and vehicle wearing parts, the system can also measure the composition of vehicle exhaust gases under actual driving conditions. Thus PMx emissions of the vehicle can be measured under actual driving conditions. REAL can measure PMx resuspension behind both wheels simultaneously. This opens a future opportunity to study whether PMx emission numbers depend on sampling point location (middle or edge of the road) and to simultaneously study different tyre types. REAL adds the capability of real-time measurement of tyre and pavement temperature. This gives an opportunity to evaluate the effect of temperature on PMx formation. Until now the relationship between temperature and PMx formation has only been confirmed in laboratory conditions. (Dahl et al., 2006). The present test with summer tyres showed that vehicle speed affects tyre temperature (Figure 6), but there was no correlation between any measured particulate fraction and tyre temperature. Between vehicle speed and tyre temperature was weak polynomial correlation (R^2=0.51) (Figure 6), the tyre temperature rose at the beginning rapidly from 27 °C up to 35 °C and after that the slower tyre heating process continued. At the end of the test (180 km highway with 100 km h^{-1} speed limit, driving time 2 hours and 30 minutes) the tyre temperature rose up to 42 °C. During the test the ambient temperature ranged between 22 to 27 °C. Heat is generated in tyres mainly because of the friction between molecules, when the rubber in the structure of the tyre is under a kinematic deformation by a continuous compression-tension or torsion (Oh et al., 1995). If the heat generation is faster than it can be transferred into the ambient air, it gradually builds up in the tyre and reaches its maximum at the outermost ply or belt (Netscher et al., 2008). Relationship between vehicle speed and tyre temperature was also observed by Dahl et al. (2006) and they

have found that increased temperature leads to increased emissions of loosely bound reinforcing filler material and evaporation of semi-volatile softening oils. Additionally Dahl et al. (2006) have stated that the properties of the oil mixture may determine whether or not homogeneous nucleation of gaseous precursors can produce significant quantities of nanometer-sized particles. In our test we could not observe any relationship between nanometer-size particles and vehicle speed. Probably the tyre temperature didn't reach the necessary temperature where the loosely bound material will start to evaporate. It may be that also the age of the tyre plays an important role in this case. Further research is needed to investigate the nanometer-size particles formation from the tyre material.

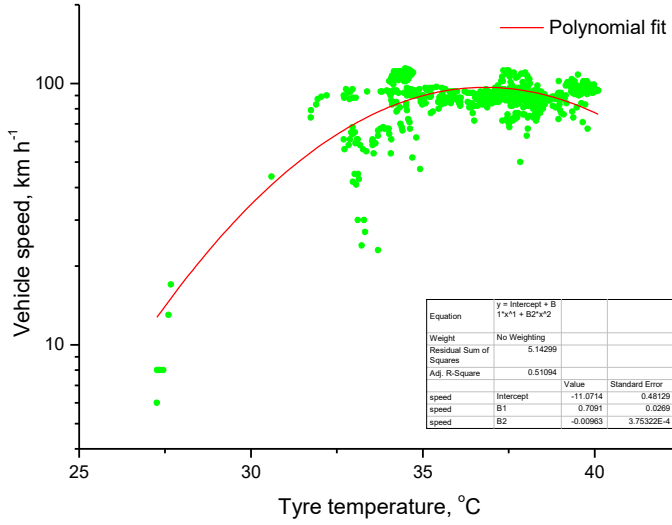

Figure 6. Vehicle speed and tyre temperature dependency graph

Test measurements showed that losses in the measurement system ranged from 2.4% ($PM_{1.0}$) to 46% (PM_{10}). Sampling losses may be expected to be greater for coarser particles, leading to an underestimation of coarse particle emissions (Thorpe and Harrison, 2008). Nevertheless, PMx losses have to be taken into account in case of longer sampling probes.

There are plans to equip REAL with sensors for measuring continuously pavement humidity, as humidity can affect formation and liftoff of fine particulates (Bukowiecki et al., 2010). A humidity sensor has so far not been added due to lack of a suitable sensor; the authors have not found a suitable sensor capable of real-time detection of pavement humidity without contact with the surface.

Comparability of measurement results is also complicated by lack of uniform standards for measured PMx size distribution and measurement method. Many similar measurements have been done with optical analyzers with an around 300 nm lower end of PMx size resolution, while for instance ELPI+ and SMPS analysers can measure considerably smaller size fractions of fine particulates.

This study showed that vehicles mostly produce coarser particles with an aerodynamic diameter between 1 and 8 µm. Various studies on health effects (Delfino et al., 2005; WHO, 2005), have concluded that finer particle fractions are the ones with the greatest effect on human health, as

they can penetrate deeper lung alveoli and move on into bloodstream from there. Therefore EF of finer fraction should receive most of the attention. PMx proportion originating from tyre wears needs to be clarified. One option for this is the measurement of marker compounds. The proportion of PMx originating from worn rubber in the samples can be assessed by later analysis of filters. Two marker compounds suggested for identifying abraded tyre material are 24MbOT (2-(4-Morpholinyl) benzothiazole) and NCBA (N-cyclohexyl-2-benzothiazolamine) (Pan et al., 2012).
Before each measurement, pavement type and condition needs to be thoroughly studied and characterized, as pavement type and condition can affect PMx formation (Blomqvist et al., 2013).
Results show that higher vehicle speed produces larger amounts of non-tailpipe emissions. Fine particulate EF depends on tyre type, winter tyres produce more of fine particulates. These results are consistent with earlier studies (Hussein et al., 2008; Mathissen et al., 2012; Pirjola et al., 2009), which further confirms suitability of REAL for such measurements.

4 Conclusions

The subject matter of the study continues to be important, as economic growth brings increased use of transport vehicles, and while gaseous emissions of vehicles are controlled via regulation, the resuspended emissions from road surface are mostly not regulated. The PMx does not only present physical hazards, fine particulates usually also carry chemically harmful substances (heavy metals, PAH). Therefore future studies should also focus on chemical analysis of fine particulate fractions.
Test measurements with REAL logged data about tyre and road surface temperature, background air fine particulates concentration, vehicle location and speed, and fine particulates emission from tyre, brake pad and road pavement abrasion. Background concentrations of fine particulates and concentration peaks caused by passing vehicles or roadside sources (dust-producing farming activities, unpaved side roads etc) were removed from the results during subsequent data analysis. Tests with studded and non-studded tyres were done in April 2013. Tests with summer tyres were done in July-August 2013. Test measurements showed that the loss of PM_{10} fraction in the measurement system's probe is around 46%. This loss was taken into account when calculating EF. We observed between vehicle speed and tyre temperature weak polynomial correlation.
Based on the results of this study, it can be concluded that the developed measurement system, REAL, is suitable for measurement of fine particulate emission originating from tyre, brake pad and pavement wear in road transport. Results of the study are consistent with published results produced with similar mobile labs.
Test measurements with the REAL system showed that it can adequately evaluate PMx emissions using different tyre types. Test measurements identified a significant relationship between vehicle speed, tyre type and fine particulates emission, which agrees with earlier studies (Hussein et al., 2008; Mathissen et al., 2012; Pirjola et al., 2009). Results show that the PM_{10} EF is the greatest with studded tyres, at speeds above 50 km h^{-1}. This is predominantly caused by greater abrasion of road surface by studded tyres, and the studs' own wear in this process. High EF of non-studded tyres is primarily caused by their softer material compared to summer tyres and resulting greater wear.
Objectives of the study were attained. It can be concluded that the REAL measurement system can measure fine particulate emissions generated by traffic and can be used for future studies. In the future, REAL might be fitted with a pavement humidity measurement equipment to study if and how pavement humidity affects fine particulate formation. In addition, fine particulate emissions should be studied on unpaved roads and general focus pointed at pavement types in

Estonia and their potential effect on fine particulate emission. Furthermore, further research is needed to investigate the nanometer-size particles formation from the tyre material.

Acknowledgments

We would like to thank Estonia's Ministry of Environment and Estonia's Ministry of Education for providing resources to V. Kimmel and M. Maasikmets with targeted financing project SF1090050s07.

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IV

Kaasik, A.; **Maasikmets, M.** (2013). Concentrations of airborne particulate matter, ammonia and carbon dioxide in large scale uninsulated loose housing cowsheds in Estonia. Biosystems Engineering, 114(3), 223–231.

Available online at www.sciencedirect.com

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Research Paper

Concentrations of airborne particulate matter, ammonia and carbon dioxide in large scale uninsulated loose housing cowsheds in Estonia

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ARTICLE INFO

Article history:
Received 22 March 2012
Received in revised form
18 December 2012
Accepted 4 January 2013
Published online 31 January 2013

The concentration of airborne particulate matter in large scale uninsulated loose housing cowsheds was investigated. Airborne particulate matter can be a potential risk factor for human and animal health. Also investigated were correlations between indoor particulate matter, noxious gas concentrations and other microclimate parameters. Measures of inhalable particulate matter (PMtotal, PM10) and respirable particulate matter (PM2.5 and PM1.0), carbon dioxide (CO_2) and ammonia (NH_3) concentrations, air temperature, and relative humidity were taken at eight to 13 locations in nine large uninsulated loose housing cowsheds in Estonia from September 2008 to August 2009. The mean recorded concentrations of PMtotal were 205 ± 270 μg m^{-3}, PM10 65 ± 121 μg m^{-3}, PM2.5 18 ± 46 μg m^{-3} and PM1.0 10 ± 11 μg m^{-3}. The overall mean inside air CO_2 concentration was 553 ± 315 ppm, and that of ammonia 1.2 ± 1.9 ppm. The mean air temperature was 9.6 ± 6.6 °C, and relative humidity 83.2 ± 16.8%. The concentration of particulate matter (all fractions) inside the uninsulated loose housing cowsheds was low compared to pig and poultry housing systems. There was a clear seasonal variation between measurements in summer and winter. The particulate matter (all fractions) and CO_2 concentrations were higher, and ammonia concentrations lower, in the winter. The particulate matter concentration in the atmosphere also had an effect on the internal environment in uninsulated loose housing cowsheds.

1. Introduction

Fine respirable airborne dust is considered to be a potential risk factor for animal and human health, as dust may penetrate into the alveoli through the respiratory tract (Carpenter, 1986; Donham, 2000; Radon et al., 2001). In livestock production, intensive poultry and pig houses are the main sources of particulate matter emissions, contributing about 50% (poultry) and 30% (pigs) of total particulate matter emissions from agriculture in Europe (EMEP–CORINAIR, 2007). The situation in Estonia may be different because most livestock production involves intensive dairy production. In Estonia there are more than 150 large scale dairies, less than 50 large scale pig and only seven large scale poultry farms (Statistics Estonia, 2011).

Dust in livestock buildings is comprised of feed and other plant-derived fractions, epithelial cells detached from the

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http://dx.doi.org/10.1016/j.biosystemseng.2013.01.002

Nomenclature

Abbreviations

CORR	correlation
EU	European Union
PMtotal	total inhalable particulate matter
PM10	inhalable particulate matter with diameter ≤10 μm
PM2.5	respirable particulate matter with diameter ≤2.5 μm
PM1.0	respirable particulate matter with diameter ≤1.0 μm
ppm	parts per million
TMR	total mixed ration
UNECE	United Nations Economic Commission for Europe

animal body, urine, faeces, micro-organisms and other particles (Dawson, 1990; Pearson & Sharples, 1995). The composition of particulate matter differs between species. For pigs, the bulk of particulate matter (PM) comes from feed (Aarnink, Roelofs, Ellen, & Gunnink, 1999; Donham, Popendorf, Palmgren, & Larsson, 1986; Takai et al., 1998). Faecal PM is also an important contributor to PM in pig rearing. Faecal PM is found to a greater extent in the respirable fraction, indicating a potential high risk to the alveoli in the lungs (Donham et al., 1986). In broiler houses, down feathers, mineral crystals from urine and litter are the main PM sources (Aarnink et al., 1999). In layer houses, skin, feathers, faeces, urine, feed and litter, are amongst the most important sources of PM (Qi, Manbeck, & Maghirang, 1992). Other livestock production systems may contribute other relevant sources of PM different from these. For instance, bedding material can contribute considerably to PM (Aarnink, Stockhofe-Zurwieden, & Wagemans, 2004) and type of litter and moisture content may also affect PM concentrations (Kaliste, Linnainmaa, Meklin, Torvinen, & Nevalainen, 2004). Gaseous compounds such as ammonia and odours in livestock housing can be adsorbed onto dust particles. Particles can carry NH_3 for a long time, and can adsorb large amounts of NH_3 (up to 7 μg NH_3 per mg of respirable PM; Takai et al., 2002). The amount of NH_3 adsorbed onto particles in livestock houses, mainly in PM2.5, can contribute 24% of the total NH_3 in the gas phase (Reynolds et al., 1998). Bacteria and viruses attached to dust particles may spread for long distances and cause infectious and allergic diseases in farm animals and humans.

The formation of PM, its concentration and emission from livestock houses, depends on many physical and biological factors (Cambra-Lopez, Aarnink, Zhao, Calvet, & Torres, 2010; Cambra-Lopez, Torres, Aarnink, & Ogink, 2011). The concentration of PM in livestock houses depends, in addition to the animal species, also on the housing system, season and within-day sampling period (Ellen, Bottcher, von Wachenfelt, & Takai, 2000). Also of importance are animal activities, animal stocking density and moisture conditions (Costa, Borgonovo, Leroy, Berckmans, & Guarino, 2009). A relative humidity of 70% and above may contribute to low PM concentrations due to high equilibrium moisture content (Takai et al., 1998). In broiler houses, total PM concentrations are significantly influenced by temperature and relative humidity (Vucemilo et al., 2008). Ventilation rate, which is also related to temperature and humidity, is an important factor, because it determines to a large extent particle formation, particle concentrations and emissions, and especially their distribution in the airspace of livestock houses (Puma, Maghirang, Hosni, & Hagen, 1999). The microclimate of uninsulated large scale dairy farms is strictly related to outside environmental factors (Pajumägi, Poikalainen, Veermäe, & Praks, 2008), thus it can be assumed that this also affects the concentration of airborne dust particles. Ventilation rates, which are related to climate and season, also affect PM concentrations inside farms. Because of higher ventilation rates in the summer compared to the winter, low PM concentrations and high emission rates can be expected in the summer, whereas high PM concentrations and low emission rates can be expected in the winter (Hinz & Linke, 1998; Redwine, Lacey, Mukhtar, & Carey, 2002). During the day farm animals are more active during daylight, when feeding and most farm activities take place. Animal movement causes local turbulence and dispersal of PM from building surfaces, causing an increase in the PM concentration (Takai et al., 1998). Reported concentrations of inhalable and respirable PM (mg m^{-3}) found in livestock houses are shown in Table 1. There is little experimental data concerning indoor inhalable airborne particle concentrations, particularly respirable airborne particles (<2.5 μm), from large scale uninsulated loose housing dairy farms. In order to assess the environmental impact of the current dairy farms it is necessary to determine their emissions.

Verified emissions are needed for annual emission reporting at the local scale (farmers, local authorities) and also at the global scale (e.g. European Union (EU), UNECE). Emissions from dairy farms in Estonia may differ from emissions from other regions in Europe due to the differences in climatic conditions and housing systems in use. There are a few research papers (Pajumägi et al., 2008; Teye, 2008; Teye et al.; 2008) regarding NH_3 and PM emissions from dairy farming in Estonia and the impact of microclimatic conditions on thermal comfort and health parameters of dairy cows has also been previously established (Pajumägi, Veermäe, Praks, Poikalainen, & Miljan, 2007) but we know of no papers concerning uninsulated loose housing and large scale farms.

Uninsulated dairy buildings have indoor temperatures similar to those outside. They are usually ventilated naturally with little or no ventilation control. Air enters the uninsulated buildings through open sidewalls, and escapes through ridge openings in the roof. Curtains, removable or hinged panels, sliding doors, or hinged windows serve as sidewall and end-wall enclosures. CO_2 measurements are important for the estimation of the ventilation rate of a loose housing system.

Large scale dairy farms, in the Estonian context, are farms with 300 or more dairy cows (plus young stock). There is no regulation regarding emissions at the EU level for intensive cattle rearing (dairy production) comparing with pigs and poultry (IPPC, BREF, 2003).

Table 1 – Measured inhalable and respirable PM concentrations in livestock houses.

Animal type	Housing system	Inhalable PM (mg m^{-3})		Respirable PM (mg m^{-3})		Reference
		Mean	Range	Mean	Range	
Broilers	Litter	10.1	–	0.10	–	Wathes, Holden, Sneath, White, and Phillips (1997)
Broilers	Litter	7.15	3.83–10.36	0.81	0.42–1.14	Takai et al. (1998)
Broilers	Litter	4.32	2.27–8.58	0.84	0.30–1.80	Banhazi, Seedorf, Laffrique, and Rutley (2008)
Layers	Cages	1.7	–	0.10	–	Wathes et al. (1997)
Layers	Litter	2.8	–	0.17	–	Wathes et al. (1997)
Layers	Cages	1.22	0.75–1.64	0.14	0.03–0.23	Takai et al. (1998)
Layers	Litter	5.28	2.19–8.79	0.84	0.35–1.26	Takai et al. (1998)
Sows, weaners, fatteners		2.19	1.87–2.76	0.23	0.18–0.26	Takai et al. (1998)
Fatteners–finishers		–	0.79–1.91	–	0.09–0.30	Gustafsson (1999)
Finishers		–	0.42–6.86	–	0.04–0.44	Schmidt, Jacobson, and Janni (2002)
Fatteners–finishers		–	2.08–5.67	–	0.16–0.71	Aarnink et al. (2004)
Fatteners		–	0.4–3.7	–	0.00–0.85	Haeussermann, Fisher, Jungbluth, Baur, and Hartung (2006)
Cows, calves, beef		0.38	0.22–0.65	0.07	0.04–0.15	Takai et al. (1998)
Cows	Cubicles	0.26	0.14–0.40	0.02	0.00–0.04	Kaasik and Maasikmets (2009)

In the last decade about 150 Estonian dairy farms were built or renovated according to the conditions described above. The main feeding method is total mixed ration (TMR), and manure is removed for storage in liquid form. The use of bedding materials is low or it is not used at all.

Therefore the objectives of this paper were to measure inhalable and respirable particle concentrations, NH_3 and CO_2 concentrations in a loose housing system under typical Estonian conditions.

2. Materials and methods

Estonia is in a temperate climate zone. The annual mean air temperature is 5 °C. Commonly the coldest month is February with a mean temperature of −5 °C, and the warmest month is July with a mean temperature of 18 °C. The annual mean relative humidity is about 80–83% (EMHI, 2011).

Microclimate parameters (temperature, °C, relative humidity, %); CO_2 and NH_3 concentration (ppm) as well as inhalable (PMtotal, PM10) and respirable (PM2.5, PM1.0) particulate matter concentrations (μg m^{-3}) were measured on nine large uninsulated loose housing cowsheds on five dairy production units in Estonia, once per month, over the period from September 2008 to August 2009. Two units were located in central Estonia, one in the north, one in the northeast and one in the eastern part of Estonia. The buildings under investigation were all built during the last five years. The lengths of the barns varied from 132 m to 160 m, breadths from 30 m to 34 m, heights of the ridge from 9.3 m to 14.2 m and heights of the surrounding walls from 3.2 m to 5.5 m (Fig. 1). On all the farms, similar feeding (TMR), manure removal (manure scraper, Fig. 2) and milking methods (milking parlour) were used. The number of cows in the buildings varied between 300 and 600. The 1-min mean concentrations of inhalable and respirable particles, CO_2 and NH_3 were measured at a 1 m height from the floor, at eight to 13 locations, depending on the size of the building, for a period of 10 min per measuring point (Fig. 3). The total time period for sample collection ranged from 1.2 to 2.5 h per cowshed. The concentrations of inhalable particles and their fine fractions were recorded at the same time. Measurements were performed in the daytime, while the cows were most active and while different work routines (TMR feeding, manure removal) were being carried out. The inside air concentration of CO_2 provided the basis for indirect assessment of the effectiveness of the ventilation in the dairy buildings, *i.e.* lower CO_2 emissions indicated a higher ventilation rate within the cow house.

A Grimm 1.108 portable aerosol spectrometer, minimum detection limit for particles with diameter to 0.23 μm (Grimm Aerosol Technik GmbH and Co, Ainring, Germany) was used for the measurements of the concentrations of airborne dust particles, and a Dräger X-am 7000 multigas detector, minimum detection limit for NH_3 1 ppm and for CO_2 300 ppm (Drägerwerk

Fig. 1 – Typical large scale uninsulated loose housing cowshed in Estonia (Photo: Aino Nõmmeots).

Fig. 2 – Interior of large scale uninsulated loose housing cowshed (Photo: Aino Nõmmeots).

AG, Lübeck, Germany) for recording gas concentrations. In all the buildings the temperature and relative humidity were constantly recorded at intervals of 15 min throughout the period of the experiment using a Rotronic HygroLog data logger (Rotronic AG, Bassersdorf, Switzerland). On two of the farms the PM10, PM2.5 concentrations and climate parameters were simultaneously recorded in the outside air for comparison from the Tartu ambient air monitoring station of the Estonian Environmental Research Centre (ca 5 km South–East of cowshed no 8 and 6.5 km East of cowshed no 4). For PM10 and PM2.5 ambient measurement a BAM 1020 (Met One Instruments Inc., Grants Pass, OR, USA) was used, which measures ambient particulate concentrations using beta ray attenuation within a range of 1 μg m^{-3} to 1.000 μg m^{-3} for 1 h.

Statistical variation between the air quality data was analysed using the SAS procedure; the SAS procedure CORR to calculate Spearman rank correlation coefficients was used. Spearman rank correlations were used as these coefficients do not assume normality of the data and are able to measure not only linear but also a more general monotonic relationship (SAS Institute Inc., 2003).

3. Results and discussion

The results are shown in Table 2 (PM) and Table 3 (CO_2, NH_3). The mean particulate matter concentration (Fig. 4a) in loose housing dairy farms during the measuring period was 205 μg m^{-3}, but this had a wide monthly range from 130 to 313 μg m^{-3}. The mean inhalable airborne particle (PM10) concentration (Fig. 4b) was 65 μg m^{-3}, with a monthly range of between 27 and 123 μg m^{-3}. The mean respirable airborne particle (PM2.5) concentration (Fig. 4c) was 18 μg m^{-3}, with a monthly range of between 7 and 32 μg m^{-3}, and the respirable airborne particle fraction PM1.0 concentration (Fig. 4d) was 10 μg m^{-3}, with a monthly range of between 3 and 20 μg m^{-3}. The uninsulated loose housing large-scale farms showed lower inhalable and respirable airborne particles concentrations compared with insulated farms with tied housing, for example 380 μg m^{-3} and 70 μg m^{-3} respectively (Takai et al., 1998; Wathes et al., 1998). This might be associated with the amounts of litter used on the farms. In contrast to cattle buildings in which cows are kept tethered, where substantial volumes of bedding material are used and renewed on a daily basis, loose housing on large scale dairy farms operate with minimal litter, or without any bedding at all. Also, in large scale uninsulated loose housing farms, the distribution of litter is carried out according to need, usually once a week.

The CO_2 concentration in the indoor air of the dairy buildings was directly affected by the outdoor environmental conditions. The more frequently the curtain walls and other ventilation outlets were opened, the greater was the volume of the air that passed through the building, and the lower was the concentration of CO_2. The mean CO_2 concentration of the indoor air (Fig. 4e) was 553 ppm and the monthly range from 313 to 822 ppm. The concentration of NH_3 in indoor air was affected primarily by the indoor temperature and ventilation rate. The mean NH_3 concentration (Fig. 4f) of the indoor air was 1.2 ppm, with a monthly range between 0.24 and 2.38 ppm. The indoor air temperature of an uninsulated cattle building is directly related to the external temperature (Pajumägi et al., 2007). The overall mean temperature (Fig. 4g) was 9.6 °C, with a monthly range from 2.0 to 20.4 °C. The overall mean relative humidity (Fig. 4h) was 83%, with a monthly range between 60 and 96%.

There was a clear seasonal variation between summer and winter. In the summer (from May to September) the concentration of the different PM fractions, CO_2 and relative humidity inside the uninsulated loose housing cattle buildings was lower than in the winter. Similar results for higher PM aerosol concentrations in the winter period were reported by Purdy, Clark, and Straus (2009). However, the temperatures and the NH_3 concentrations were higher. Also, the

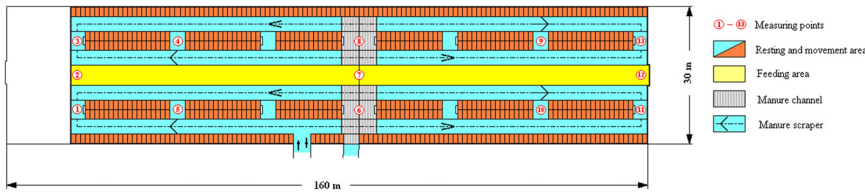

Fig. 3 – Plan of the cowshed with 13 measurement points indicated.

Table 2 – Descriptive statistics of particulate matter (PMtotal and fractions PM1.0, PM2.5, PM10) concentration per farm investigated.

Farm no	PMtotal				PM1.0				PM2.5				PM10			
	$\mu g\ m^{-3}$				$\mu g\ m^{-3}$				$\mu g\ m^{-3}$				$\mu g\ m^{-3}$			
	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max
1	345.3	428.3	5.6	1849.4	12.1	12.5	1.9	47.3	21.7	24.5	3.0	264.9	119.5	160.8	5.6	916.2
2	212.3	259.1	12.8	2268.0	9.5	11.0	2.0	91.4	19.0	52.5	3.2	982.2	69.2	106.9	8.8	1520.9
3	201.9	202.5	8.0	1290.9	7.7	6.4	1.8	39.8	13.6	20.1	2.4	336.7	66.3	76.8	6.8	647.2
4	159.2	136.6	5.5	1078.2	12.6	15.0	0.9	96.4	19.2	23.9	2.0	285.5	49.3	56.8	5.5	911.6
5	310.4	199.2	14.9	1839.9	11.2	10.5	1.6	76.6	23.6	39.1	3.6	485.4	96.1	86.4	14.9	882.4
6	128.1	190.3	3.5	2186.1	10.0	8.6	1.3	77.9	16.6	36.4	2.1	681.2	41.8	131.1	3.5	1908.0
7	205.3	201.6	10.2	1525.1	9.5	12.4	0.8	77.1	17.4	28.9	1.7	324.2	64.2	105.1	8.2	983.6
8	160.9	136.7	9.0	1081.3	8.6	10.9	0.7	46.6	16.2	41.3	1.1	787.4	40.0	52.6	4.5	806.4
9	125.0	133.2	3.0	1623.4	7.8	10.0	0.5	87.8	14.3	42.3	1.1	761.9	38.3	119.6	3.0	2177.1

variation within parameters between these months within the summer period was smaller than in the winter. Such seasonal variations of PM and the main microclimate parameters are also typical for pig houses (Costa & Guarino, 2009).

Pearson correlation coefficients of the results (Table 4) showed that the concentrations of PM1.0, PM2.5 and PM10 in uninsulated loose housing cowsheds were positively correlated with the total particulate matter concentration. A quantity of PM, especially the fine fractions, can pass into the uninsulated cattle building from the external environment: for example from gravel roads nearby, industrial activities or automotive emissions (Purdy et al., 2009).

There was also a strong positive correlation between the concentrations of all particulate matter fractions and CO_2 concentration – the lower the ventilation rate (higher CO_2 concentration), the higher the concentration of PM particles of different fractions. The NH_3 concentration in the air inside the cowsheds was most strongly correlated with the concentrations of the fine fractions of PM. A similar tendency has been observed by others (Reynolds et al., 1998; Takai et al., 2002). No significant relationships were found between the total concentration of PM and either the indoor temperature or the relative humidity in the cowsheds. However, when the temperature and relative humidity increased, the concentration of total particulate matter concentration decreased; there was weak negative correlation between these parameters. A rise in indoor temperature significantly reduced the concentrations of PM1.0; PM2.5 and PM10 (there was a strong negative correlation). There was also a strongly negative correlation between the indoor temperature and CO_2 concentration. This is logical as, with an increase in temperature, the wall curtains will be opened and a higher ventilation rate will be achieved (and the CO_2 concentration will decrease). The temperature and NH_3 concentrations inside the cattle buildings were positively correlated. As the NH_3 is a result of microbial processes, then a higher than optimal temperature would stimulate NH_3 production. Carbon dioxide and NH_3 concentration was weakly positively correlated. A larger volume of air inside the building also dilutes the NH_3 concentration. Similar results were reported by Bluteau, Masse, and Leduc (2009) for tie-stall dairy buildings. There was a strong negative correlation between indoor temperature and humidity; an increase in the indoor temperature decreased the relative humidity.

Table 3 – Descriptive statistics of carbon dioxide and ammonia concentration per farm investigated.

Farm no	CO_2			NH_3		
	ppm			ppm		
	Mean	SD	Max	Mean	SD	Max
1	500	212	1091	1.6	1.7	7.9
2	508	250	1943	1.3	1.8	8.2
3	507	230	1563	1.4	2.3	14.8
4	639	415	2010	1.6	2.9	22.1
5	760	453	3006	1.9	2.1	9.5
6	479	244	1871	0.6	1.3	7.9
7	538	235	1438	1.3	1.7	9.9
8	532	211	1648	0.8	1.2	7.1
9	517	254	1813	0.7	1.2	10.6

The correlation between the particulate matter concentrations and the relative humidity inside the cattle buildings is of interest. While the total PM concentration was weakly negatively correlated with relative humidity, the PM10, and especially the PM2.5 and PM1.0, were strongly positively correlated with the relative humidity. A possible explanation is that the coarse, mostly solid, fractions clump together in moist environments, into larger particles and precipitate to the ground. However, the finest fractions of PM contain a large proportion of liquid components (water vapour and compounds incorporated with water). The higher moisture inside the cowshed was accompanied by a higher concentration of CO_2. No correlation between the concentration of moisture and NH_3 was detected.

The concentration of particulate matter (PM10 and PM2.5) inside the loose housing cowsheds depends a great deal on the particulate matter concentration of the outdoor air. Figures 5 and 6 show how the PM10 and PM2.5 concentrations inside and outside were related. The finer the particles the more they are carried into the cowshed from outside. The correlation between the inside and outside concentrations is stronger for fine fractions, $r = 0.208$ (PM10) and $r = 0.365^{**}$ (PM2.5) respectively. Therefore, the coarser normally heavier

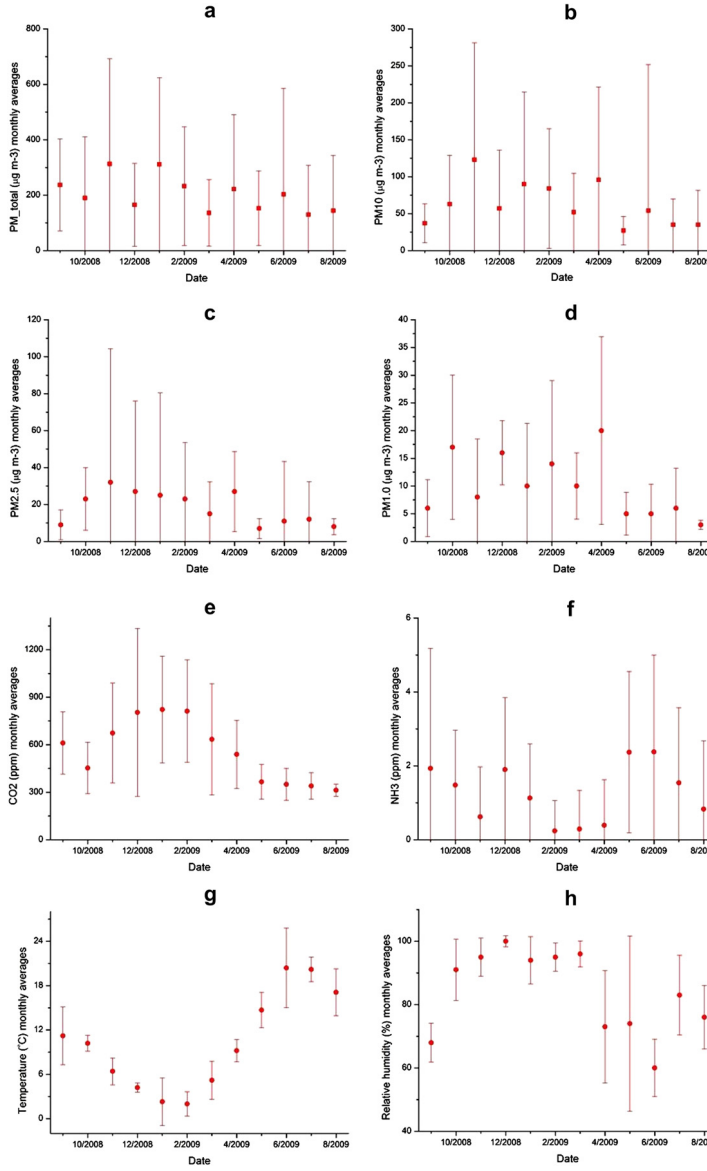

Fig. 4 – Mean values of measured parameters. (a) PMtotal, (b) PM10, (c) PM2.5, (d) PM1.0, (e) CO_2, (f) NH_3, (g) indoor temperature, (h) relative humidity.

Table 4 – Correlations between measured variables.

Variable	PMtotal	PM1.0	PM2.5	PM10	CO_2	NH_3	Temp	RH
	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	ppm	ppm	°C	%
PMtotal	–	$r = 0.174$	$r = 0.379$	$r = 0.796$	$r = 0.395$	$r = 0.045$	$r = -0.136$	$r = -0.135$
$\mu g\ m^{-3}$		$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P = 0.012$	$P = 0.250$	$P = 0.346$
PM1.0	$r = 0.174$	–	$r = 0.886$	$r = 0.491$	$r = 0.377$	$r = 0.205$	$r = -0.263$	$r = 0.544$
$\mu g\ m^{-3}$	$P < 0.0001$		$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P = 0.025$	$P < 0.0001$
PM2.5	$r = 0.379$	$r = 0.886$	–	$r = 0.727$	$r = 0.403$	$r = 0.155$	$r = -0.346$	$r = 0.560$
$\mu g\ m^{-3}$	$P < 0.0001$	$P < 0.0001$		$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P = 0.0027$	$P < 0.0001$
PM10	$r = 0.796$	$r = 0.491$	$r = 0.727$	–	$r = 0.463$	$r = 0.086$	$r = -0.261$	$r = 0.191$
$\mu g\ m^{-3}$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$		$P < 0.0001$	$P < 0.0001$	$P = 0.0258$	$P = 0.1785$
CO_2	$r = 0.395$	$r = 0.377$	$r = 0.403$	$r = 0.463$	–	$r = 0.013$	$r = -0.691$	$r = 0.584$
ppm	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$		$P = 0.4462$	$P < 0.0001$	$P < 0.0001$
NH_3	$r = 0.045$	$r = 0.205$	$r = 0.155$	$r = 0.086$	$r = 0.013$	–	$r = 0.355$	$r = -0.098$
ppm	$P = 0.012$	$P < 0.0001$	$P < 0.0001$	$P < 0.0001$	$P = 0.4462$		$P = 0.0024$	$P = 0.4963$
Temp	$r = -0.136$	$r = -0.263$	$r = -0.346$	$r = -0.261$	$r = -0.691$	$r = 0.355$	–	$r = -0.542$
°C	$P = 0.250$	$P = 0.025$	$P = 0.0027$	$P = 0.0258$	$P < 0.0001$	$P = 0.0024$		$P < 0.0001$
RH	$r = -0.135$	$r = 0.544$	$r = 0.560$	$r = 0.191$	$r = 0.584$	$r = -0.098$	$r = -0.541$	–
%	$P = 0.346$	$P < 0.0001$	$P < 0.0001$	$P = 0.1785$	$P < 0.0001$	$P = 0.496$	$P < 0.0001$	

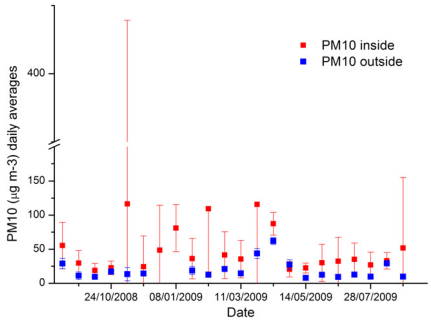

Fig. 5 – The concentration of PM10 inside and outside uninsulated loose housing cowsheds.

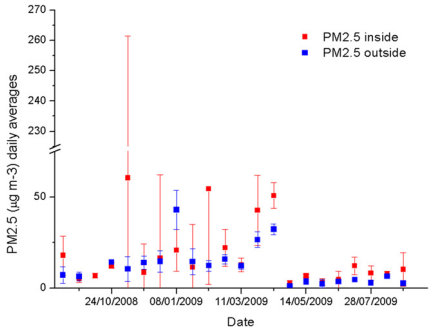

Fig. 6 – The concentration of PM2.5 inside and outside uninsulated loose housing cowsheds.

particles precipitate more rapidly. The fluctuation of the PM concentration inside the cowshed was primarily a result of animal activity and management routines.

4. Conclusions

The mean total PM concentration was 0.21 mg m^{-3}; that of PM10 was 0.07 mg m^{-3}; of PM2.5 was 0.02 mg m^{-3} and of PM1.0 was 0.01 mg m^{-3}, respectively. A seasonal variation between summer and winter was shown. During the winter PM (all fractions) and CO_2 concentrations were higher, and NH_3 concentration lower. There was also a strong positive correlation between the concentrations of all particulate matter fractions and the CO_2 concentration. Ammonia concentration was associated most strongly with the concentration of fine fractions of PM. No statistically significant relationship was found between the concentration of total PM and the indoor temperature and relative humidity. An increased indoor temperature significantly reduced the concentrations of PM1.0; PM2.5 and PM10. The correlation between the indoor temperature and CO_2 concentration was also strongly negative. The indoor temperature and the NH_3 concentration were positively correlated. While the total PM concentration had a weak negative correlation with relative humidity, the PM10, but especially PM2.5 and PM1.0, had strong positive correlations with relative humidity. There was no correlation between the relative humidity and NH_3 concentration. The finer the particles the more likely they are to pass into the cowshed from outside. The correlation between the inside and outside PM concentrations was strongest for the fine fractions.

Acknowledgement

This work was supported by the Estonian Ministry of Education and Science, project SF 0170165s08.

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CHAPTER 6

Seasonal variability of the PM and ammonia concentrations in uninsulated loose-housing cowshed

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6.1 INTRODUCTION

Air pollution is part of the impact that agricultural activity has on the environment. The large number of animals raised in concentrated animal feeding operations can affect air quality by emissions of odor, volatile organic compounds (VOCs) and other gases, and particulate matter (PM) (NRCNA, 2003). Livestock production is a major contributor to ammonia emissions (Groot Koerkamp *et al*., 1998; Steinfeld *et al*., 2006). Ammonia released from near-surface sources into the atmosphere generally has a relatively short lifetime of 1–5 days and may deposit near the source through dry or wet deposition processes. However, ammonia can also participate in atmospheric reactions (e.g., gas-to-particle conversion) once airborne, forming ammonium aerosols such as ammonium sulfate, ammonium nitrate and ammonium chloride, which tend to have longer atmospheric residence lifetimes (1–15 days) due to a decrease in dry deposition velocity (Aneja *et al*., 2001) and may, therefore, be transported and deposited further downwind from the source (Blunden *et al*., 2008). Gaseous ammonia emissions from livestock production are deemed responsible for the acidification of several ecosystems and for the formation of secondary particulate matter (PM2.5) (Bluteau *et al*., 2009). The presence of ammonium sulfate in the air is an important mitigation impact for ammonia because particles can stay in the air for several days and cause decrease visibility (USEPA, 2001). High concentrations of PM can threaten the environment, as well as the health and welfare of humans and animals.

PM in livestock houses is mainly coarse, primary in origin and organic; it can adsorb and contain gases, odorous compounds and microorganisms, which can enhance its biological effect (Cambra-López *et al*., 2010). The air inside animal houses usually contains high levels of PM (Takai *et al*., 1998). Emissions from pig and poultry houses represent around 30% and 55%, respectively, agricultural PM emissions; the remainder is mainly produced by arable farming. Livestock housing is estimated to produce between 9% and 35% of total emissions as PM10 (EEA, 2013).

Mechanical and natural ventilation systems are used in these houses to remove the heat, moisture, ammonia and carbon dioxide produced by the animals. As a result, large quantities of PM are released into the atmosphere (Winkel *et al*., 2015), which may have negative impacts on human health, as shown in many other studies (Delfino *et al*., 2005; Orru *et al*., 2011; Pope and Dockery, 2006; Pope *et al*., 2002). Fine particulates, especially very fine particulates (PM2.5 and smaller), are particularly risky to human health, causing various respiratory and cardiovascular diseases, even lung cancer (Delfino *et al*., 2005; Pope *et al*., 2002), but to date, the knowledge about the specific impacts of the livestock PM on the people and animal health has been poorly researched. Andersen *et al*. (2004) finds that the most relevant health hazards of PM inside livestock houses are related to respiratory diseases. Swine operation workers have a high prevalence of wheezing and symptoms of chronic bronchitis and an acute decrease in the lung function (Cai

et al., 2006). Wathes *et al*. (1983) found that for animals, PM of 5 μm was the critical size below which the lungs are penetrated and emphasized that the degree of hazard depends on the site of deposition, retention time and the nature of the PM. Estimates of the health impacts attributable to exposure to air pollution (including livestock farming) indicate that fine PM concentrations in 2011 were responsible for about 458,000 premature deaths in Europe (over 40 countries), and around 430,000 in the EU-28, originating from long-term exposure (European Environment Agency, 2014).

PM is not a single pollutant but a mixture of many types of pollutants. A particle can be defined as a small, discrete object and PM includes materials with particle-like properties. The term PM is often used for air quality applications to refer to fine solid or liquid particles suspended in a gaseous medium. This definition is also true for the term aerosol, although this term is more commonly used in atmospheric science (Cambra-López *et al*., 2010). Relatively higher energy processes, such as combustion, produce finer particles, while lower energy processes, for instance crushing or grinding, produce coarser particles. PM from animal feeding operations (AFOs) therefore includes both fine particles, from the engine exhaust of farm vehicles, and influences from ambient air and coarse particles, from hoof action on dry manure and soil or feed grinding. In contrast to PM in urban areas, however, coarse PM dominate AFO emissions because most are generated by lower energy mechanical processes (Auvermann *et al*., 2006).

Evaluations of PM concentrations at AFOs, therefore, are important for assessing the quality of air with respect to both human and animal health (Joo *et al*., 2013).

We have to distinguish primary and secondary PM emissions from livestock farming, because the formation pathways and probably also the effects on human and animal health are different. It is necessary on the one hand, to obtain data on three fundamental particle properties: particle morphology, primarily size and composition, to understand how PM is formed in livestock houses (Cambra-López *et al*., 2010). The main source of primary PM emission is from livestock housing buildings, although outdoor yard areas may also be significant sources. These emissions originate mainly from feed, which accounts for 80% to 90% of total PM emissions. Bedding materials such as straw, peat or wood shavings can also give rise to airborne particulates. Animal activity may also lead to resuspension of previously settled dust into the atmosphere of the livestock building (re-entrainment) (EEA, 2013). PM from housed livestock contains a much greater proportion of particles of biological origin and/or activity, usually referred to as bioaerosols, compared with urban or industrial PM (Cox and Wathes, 1995). On the other hand, secondary particles are fine, falling normally in the PM2.5 size range, and are generated from chemical reactions between gases and particles in the atmosphere. Some particles in the PM2.5 size range, however, can also be primary in origin, like particles emitted from combustion processes, rich in elemental carbon. Secondary PM is rich in sulfates (SO_4^{2-}), nitrates (NO_3^-), and ammonium (NH_4^+). Gas-to-particle conversion processes can occur to form secondary inorganic particles in the presence of certain precursor gases such as NH_3, nitrogen oxides (NO_x), sulfur dioxide (SO_2), and volatile organic compounds (VOCs) (Cambra-López *et al*., 2010). For example, NH_3 can react at high relative humidity (RH) and low temperature with the nitric acid (HNO_3) and form particulate ammonium nitrate (NH_4NO_3), which is discussed in more detail by Gupta *et al*. (2003). As NO_x are present inside the cowshed due the influence of the vehicle emissions, HNO_3 can be formed; thus, secondary particles can be formed as well. NH_4NO_3 formation is a reversible reaction, with an equilibrium constant dependent on temperature and relative humidity. In the absence of sufficient ammonia to fully neutralize sulfate, the formation of particulate ammonium nitrate is not favored. If excess ammonia is available, however, ammonium nitrate can form. (Lee *et al*., 2004).

Although knowledge about PM source profiles and chemical compositions is essential for source identification and the development of source-specific PM mitigation techniques, the study of AFO PM source apportionment and chemical speciation is very much limited (Wang-Li, 2015). Chemical compositions of PM in animal houses varied with animal species, housing type, and waste management systems (e.g., dry or wet systems, with or without bedding materials,

housecleaning methods). According to Aarnink *et al*. (1999), every kilogram of inhalable PM in swine houses contained 920 g of dry matter, 149.5 g ash, 67 g N, 14.7 g P, 27.8 g K, 7.8 g Cl, and 8.2 g Na; every kilogram of inhalable PM in broiler houses contained 911 g of dry matter, 97.4 g ash, 169 g N, 6.4 g P, 40.3 g K, 4.2 g Cl, and 3.2 g Na. Cambra-López *et al*. (2011) used particle morphological and chemical speciation data to identify and quantify the contributions of various sources to primary PM2.5 and PMcoarse (i.e., PM10–2.5) in poultry and swine production houses. They discovered that feather and manure are two major sources of PM in poultry houses, and skin and manure are major sources of PM in swine houses. Contribution from feed to both fine and coarse PM was insignificant.

PM emissions from livestock housings vary with the type of housing and livestock. To assess the impact on PM levels and the contribution to secondary PM, suitable emission factors (EF) are necessary to identify NH_3 levels in a cowshed. The aim of the current study was to create EF and an emission database for loose-housing uninsulated cowsheds, because this is the dominant type of housing used nowadays in Europe.

6.2 MATERIALS AND METHODS

Microclimate parameters (temperature, °C; relative humidity, %); carbon dioxide (CO_2) and ammonia (NH_3) concentration, in ppm, as well as the fractional distribution of particulate matter (PM) mass (μg m^{-3}) and number (1 cm^{-3}) concentrations (size classes with aerodynamic diameters less than 10.00, 8.17, 5.18, 3.12, 1.97, 1.24, 0.77, 0.49, 0.32, 0.20, 0.12, 0.07, or 0.04 μm) were measured in an uninsulated loose-housing cowshed in Märja, Estonia (Fig. 6.1). The CO_2 concentration inside the cowshed was measured to estimate the ventilation rate (m^3 h^{-1}). Measurement campaigns were carried out from 10 January 2010 until 12 February 2010 (represents winter period); 18 March 2011 until 2 May 2011 (represents spring period); and 1 February 2013 until 27

Figure 6.1. Location of the Märja cowshed.

August 2013 (represents winter, spring and summer period). Those periods were chosen to generate representative data for the cold and warm periods, as the concentrations of PM and NH_3 can vary depending on the seasonality. The total mixed ration (TMR) feeding technology was used on the farm, and the manure scraper and milking robot were used for manure removal and milking, respectively. During the measurements, the cowshed had 114 milking cows, which represented 114 livestock units (LU). The 1 min average concentrations for PM and CO_2 and the 3 s average concentrations for NH_3 were measured continuously at 2.5-m above the floor inside the barn. An electrical low-pressure impactor (ELPI, Dekati) with aa sampling rate of 29.25 L min^{-1} was used to measure mass and number concentration of the PM fractions. For the PM mass calculations, the particle average density of 1.68 g cm^{-3} was assumed, according to Cambra-López *et al*. (2011). The particles are first charged to a known charge level in the corona charger. After charging, the particles enter a cascade low-pressure impactor with electrically insulated collection stages. The particles are collected in the different impactor stages depending on their aerodynamic diameter, and the electric charge carried by particles into each impactor stage is measured in real time by sensitive electrometers. This measured current signal is directly proportional to particle number concentration and size, thus, the ELPI provides particle concentration and size distribution in real time (ELPI, 2013). At the particle inlet, the Dekati Dryer DD-600, and for removing larger particles than 10 µm (aerodynamic size) DIGITEL Low Volume Inlet DPM1003 (1.8 m^3 h^{-1}), were used. The Dekati Dryer DD-600 is a particle dryer designed to remove water in real time from an aerosol sample in air quality measurements. Since most ambient air particles are hygroscopic, they grow as the ambient humidity increases. Traditionally, this water has been removed from the particle sample after gravimetric collection by equilibration or heating of the sample. Both of these methods may also result in a loss of other volatile components from the sample, whereas the Dekati Dryer only removes water. The operation of the Dekati Dryer is based on a co-polymer Nafion tube for removing humidity from the sample (ELPI, 2013). For NH_3, the Picarro G2103 (Picarro) analyzer was used, which uses the Wavelength-Scanned Cavity Ringdown Spectroscopy (WS-CRDS), with the range from 1 ppb to 50 ppm, for NH_3 detection. For the CO_2 measurements, the CARBOCAP GMT 222 (Vaisala Oy) with the infrared (IR) sensor was used, with the range of 1 to 10,000 ppm. The temperature and relative humidity were determined at 1-min intervals with a HUMICAP HMT 130 data logger (Vaisala Oy). For data collection and management, the Hydromet MAWS 110 (Vaisala Oy) system was used. The background ambient air concentrations of PM10 and PM2.5 and the meteorological parameters were measured at the Saarejärve (58°43′39.44″, 26°30′15.56″) rural ambient air monitoring station (about 33 km north of the Märja cowshed), which is operated by the Estonian Environmental Research Centre. For the ambient PM10 and PM2.5 measurements, BAM 1020 (Met One Instruments Inc.) was used, which measures ambient particulate concentration using beta ray attenuation with 1 h resolution from 1 µg m^{-3} to 1000 µg m^{-3}.

From the measured CO_2 concentration, the ventilation rate (V) was calculated. The CO_2 balance equation is based on the conservation of mass in the building, under steady-state conditions. The CO_2 balance can be expressed by the following equation (Pedersen *et al*., 1998):

$$V = \frac{C}{\Delta C \times 10^{-6}} \tag{6.1}$$

where C is the carbon dioxide production (m^3 h^{-1}) and ΔC is the difference in carbon dioxide content between indoor and outdoor air (ppm).

The ventilation rate was calculated from Equation (6.1) assuming a carbon dioxide production per HPU (heat producing unit) of 0.185 m^3 h^{-1} (Pedersen *et al*., 1998). The ventilation rate was calculated for every 30-min data point, and the mean value with the standard deviation was found. For the EF calculation, the following equation was used:

$$EF = V \times \Delta\text{conc} \tag{6.2}$$

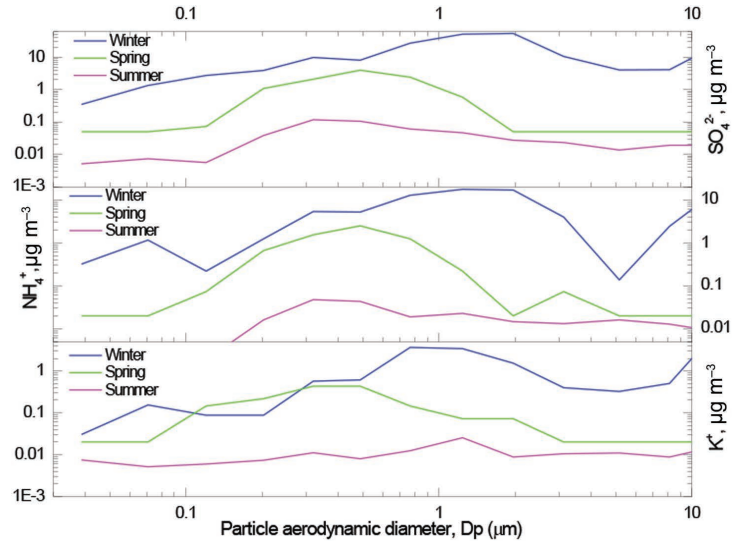

Figure 6.2. PM ionic composition during different seasons.

where Δconc is the difference in measured concentration of pollutants (µg m^{-3}) inside the barn and in ambient air.

For the NH_3 background concentration, the value from Maasikmets (2007) of 1.92 µg m^{-3} was used, which was measured within 1 month during the summer period in the rural background near Tartu.

Statistical variation between the data was analyzed by using the statistical software SPSS Statistics 17.0 (IBM SPSS Statistics), where the Bivariate Correlation procedure was used to calculate Spearman Correlation Coefficient (Spearman's rho ρ, nonparametric correlations algorithm).

6.3 RESULTS AND DISCUSSION

As fresh air to the loose-housing cowshed is flowing through the openings and, therefore, the ambient air levels influence the indoor air, it is always important to take into account the ambient air levels of PM and other pollutants, if indoor PM levels from the loose-housing cowshed are measured. The Märja cowshed is situated approximately 5 km southwest of the town Tartu (about 100,000 inhabitants). The main wind direction (blowing from) is southwest, south and during winter, mainly east, northeast (Fig. 6.1). The wind direction analysis showed that high concentrations of PM occurred mainly if the wind was blowing from east and northeast, which shows that within some periods (mainly in winter during the heating season) the cowshed was also influenced by the urban PM emissions. Episodes that were mainly caused by the high urban PM levels were extracted from the dataset. For the PM background concentrations, the Saarejärve monitoring station data was used, as the station is situated in the rural background area and the measured PM levels are representative of the PM background levels in a larger area. The Saarejärve background PM concentrations are comparable to other Estonian rural background stations like Vilsandi (58°22′34.34″, 21°50′40.69″) and Lahemaa (59°30′1.43″, 25°56′9.87″), which confirms that those stations are mainly influenced by transboundary air pollution, as important

pollution sources near stations are absent. On average, around 88% of PM10 and 83% of PM2.5 originates from the cowshed, and the rest is considered to be ambient background.

The measured concentrations and calculated EF are given in Table 6.1. The mean level of NH_3 for the whole period was 3042.98 ± 1433.93 µg m^{-3}. Teye (2008) has found that NH_3 levels remained mostly below 7000 µg m^{-3} in Finnish and Estonian dairy buildings. In the Märja cowshed, the highest NH_3 concentrations occurred during the winter period, when the concentrations were in the range 4085.25 ± 1689.08 µg m^{-3}. During winter period, the ventilation rate was the lowest and this was the main reason for the high NH_3 concentrations. During the winter period, there was a significant correlation between measured NH_3 and CO_2 concentrations (ρ = 0.556**) and between NH_3 and RH (ρ = 0.199**). During the spring period, there was a significant correlation between NH_3 and PM2.5 (ρ = 0.563**), PM10 (ρ = 0.498**), and CO_2 (ρ = 0.639**). A similar tendency was also observed by Takai *et al*. (2002), Kaasik and Maasikmets (2013). There was significant correlation between PM2.5 and PM10 and relative humidity (respectively, ρ = 0.324**, ρ = 0.336**) and CO_2 (respectively, ρ = 0.425**, ρ = 0.419**). This indicates that the NH_3 and PM concentrations are directly influenced by the ventilation rate. The temperature during all campaigns was relatively stable, on average, 16.11°C ± 2.87, and during the winter, the cowshed indoor temperature stayed around 10.10 ± 3.22°C, while ambient temperatures averaged −4.68 ± 4.81°C. PM10 and PM2.5 mass concentrations were highest during the winter period, where the ventilation rate was low. The measured mean PM2.5 mass concentrations are comparable to values from Takai *et al*. (1998), where the PM2.5 concentrations in the range of 40 to 150 µg m^{-3} were measured. Mean PM10 mass concentrations are about six times lower compared to Takai *et al*. (1998). The reasons for lower PM10 concentrations could be that a different measurement technique was used, especially the use of Dekati Dryer DD-600 before inlet, which keeps the moisture in constant level. The background concentrations of PM and NH_3 were taken into account, which was not the case in the compared literature data. An important factor influencing the results can also be that in the Märja cowshed, a minimal amount of bedding is used. The measured PM10 and PM2.5 concentrations are generally comparable with Kaasik and Maasikmets (2013), Schrade *et al*. (2014) and Winkel *et al*. (2015). According to Joo *et al*. (2013), PM10 concentrations in the barns were lowest (22–29 µg m^{-3}) in winter but averaged between 64 and 240 µg m^{-3} in the other seasons.

The mean PM2.5 and PM10 emissions (g LU^{-1} d^{-1}) were 0.192 ± 0.33 and 0.359 ± 0.481, respectively. PM emissions were higher during the winter period and lowest for PM2.5 during the summer and for PM10 during the spring period. Schrade *et al*. (2014) observed PM10 emissions in the range of 0.02 and 2.1 g LU^{-1} d^{-1}, which is generally comparable to our results. During the spring period, the highest PM2.5 and PM10 background values were observed, which is normal in Estonia because the heating season is still ongoing, and additionally after snow smelting because PM emissions from resuspension are occurring.

The PM ionic composition from ELPI filters was analyzed (Fig. 6.1). PM levels in the cowshed were more influenced during the winter and spring season by the other sources, like residential wood combustion (elevated K^+) and regional pollution (elevated SO_4^{2-} levels). Elevated NH_4^+ levels during winter can be caused by the local farm itself or by regional pollution. The formation of particulate ammonium nitrate is not favored thermodynamically during warmer periods. During the winter period, the ionic composition is the highest in the size range of 1 µm, while during the summer, the highest peak is around 0.5 µm. This indicates that during the winter period, particles inside the cowshed are more aged, which is caused by the regional pollution or due to lower ventilation rate, which causes the formation of larger particles due to longer residence time in the cowshed.

On average, the ventilation rate was 260.63 ± 12.12 m^3 h^{-1} per LU, and the highest ventilation rate occurred during the spring time. According to the survey of Seedorf *et al*. (1998) across Northern Europe, the mean ventilation rate was 341 m^3 h^{-1} for cattle, which is comparable to

** Correlation is significant at the 0.01 level (2-tailed)

Table 6.1. Mean values with standard deviation (SD) for measured and calculated values.

	Winter, mean	SD	Spring, mean	SD	Summer, mean	SD	Mean	SD
CO_2, mg m^{-3}	3087.78	961.95	1797.08	529.52	1972.26	415.24	2285.71	635.56
RH % (indoor)	66.94	10.35	60.46	11.91	70.08	10.67	58.95	11.82
Temperature, °C (indoor)	10.10	3.22	17.86	3.08	20.36	2.31	16.11	2.87
NH_3, ug m^{-3}	4085.25	1689.08	4008.23	2274.38	1035.44	338.33	3042.98	1433.93
PM2.5, µg m^{-3}	94.62	157.81	15.55	32.29	14.8	22.63	41.66	70.91
PM10, µg m^{-3}	129.91	169.22	23.03	41.47	59.22	69.68	70.72	93.46
PM2.5 background, %	8.73	5.65	24.02	14.41	17.18	10.31	16.64	10.13
PM10 background, %	7.6	5.12	22.01	13.2	6.17	3.7	11.92	7.34
Ventilation rate, m^3 h^{-1} per LU	152.69	20.4	338.62	8.7	290.59	7.25	260.63	12.12
NH_3 emission, g day^{-1} per LU	14.99	0.62	32.51	1.84	7.18	0.23	18.23	0.9
PM2.5 emission, g day^{-1} per LU	0.347	0.58	0.126	0.26	0.103	0.16	0.192	0.33
PM10 emission, g day^{-1} per LU	0.476	0.62	0.187	0.337	0.413	0.486	0.359	0.481

our result. According to Winkel *et al*. (2015) the mean ventilation rate for dairy cattle farm was 698 m^3 h^{-1} per LU, which is more than two times higher than our results, which is probably caused by the cowshed constructional differences.

According to the Estonian national emission inventory, 100,000 dairy cows are emitting 3.33 (with manure storage), 0.023, and 0.035 kilotons (kt) of NH_3, PM2.5, and PM10 per year, respectively. The calculated yearly emissions according to the average EF are given in Table 6.1: yearly emissions of NH_3 (without manure storage), PM2.5 and PM10 are 1.82, 0.019 and 0.036 kt, respectively, which is the same order of magnitude reported by the official inventory using default EF from EEA (2013). Dairy NH_3, PM2.5, and PM10 yearly emissions contributed, respectively, around 16%, 0.1%, and 0.14% to the total Estonian yearly emissions, which shows that direct PM emissions from the dairy cowsheds are negligible, but NH_3 emissions are important because NH_3 is affecting ecosystems and contributing to secondary particle formation.

6.4 CONCLUSIONS

The objective of this paper was to compare common EF for the dairy loose-house farming with the EF, which were obtained by the measurements. Microclimate parameters (temperature, °C; relative humidity, %), CO_2 and NH_3 concentrations (ppm), and particulate matter (PM10 and PM2.5) mass (µg m^{-3}) concentrations were measured in an uninsulated loose-housing cowshed in Märja, Estonia. The measurements showed that livestock housing is mainly contributing to a coarser fraction of PM. The indoor concentrations of PM2.5 were more influenced by ambient air concentrations. On average, around 88% of PM10 and 83% of PM2.5 originates from the cowshed, and the rest is considered ambient background. The NH_3 and PM concentrations were also strongly influenced by the ventilation rate: during low ventilation rates, higher concentrations were observed. The measured concentrations are generally comparable to literature values, although few papers about PM2.5 and PM10 emissions from cattle farming are available. PM ionic composition analysis showed that the cowshed indoor air was more influenced by other sources during the winter and spring season, especially by residential wood combustion (elevated K^+) and from regional pollution (elevated SO_4^{2-} levels). The measured concentrations in the

Märja cowshed are representative of the cold and warm period. Calculating the emissions based on EF from this study, we found that, in general, yearly emissions are comparable to the official emission report. PM emissions from the dairy cowsheds are negligible, but NH_3 emissions are important because they are affecting ecosystems and contributing to the secondary particle formation.

6.5 ACKNOWLEDGMENTS

We would like to acknowledge Estonia's Ministry of Education for providing resources to V. Kimmel and M. Maasikmets with targeted financing project SF1090050s07. The authors would also like to thank the staff from the Märja cowshed and the people from the Institute of Veterinary Medicine and Animal Sciences of the Estonian University of Life Sciences.

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Honours & awards

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Aser Sikk, Master's Diploma, 2015, (sup) Marek Maasikmets; Tõnis Põder, ÕHU KAUDU LEVIVATEST SAASTEAINETEST LÄHTUVA KUMULATIIVSE TERVISERISKI HINNANG MUUGA-MAARDU PIIRKONNAS (Cumulative health risk assessment of airborne pollutants in Muuga - Maardu region), Tallinn University, Institute of Mathematics and Natural Sciences, Department of Natural Sciences, Keskkonnakorralduse õppetool.

Hanna-Lii Kupri, Master's Degree, 2015, (sup) Marek Maasikmets; Viktoria Voronova, Air pollutants from the combustion of waste in the masonry stove, Tallinn University of Technology, Faculty of Civil Engineering, Department of Environmental Engineering.

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Juhendatud väitekirjad

Aser Sikk, magistrikraad, 2015, (juh) Marek Maasikmets; Tõnis Põder, ÕHU KAUDU LEVIVATEST SAASTEAINETEST LÄHTUVA KUMULATIIVSE TERVISERISKI HINNANG MUUGA-MAARDU PIIRKONNAS, Tallinna Ülikool, Matemaatika ja Loodusteaduste Instituut, Loodusteaduste osakond, Keskkonnakorralduse õppetool.

Hanna-Lii Kupri, magistrikraad, 2015, (juh) Marek Maasikmets; Viktoria Voronova, Air pollutants from the combustion of waste in the masonry stove (Jäätmete koduahjus põletamisest eralduvad saasteained), Tallinna Tehnikaülikool, Ehitusteaduskond, Keskkonnatehnika instituut.

Maria Oravas, magistrikraad, 2015, (juh) Marek Maasikmets; Arvo Iital, EMISSIONS OF AMMONIA FROM AGRICULTURAL FACILITIES AND POTENTIAL EFFECT OF NITROGEN ON NATURA 2000 AREAS IN ESTONIA (Ammoniaagi heitkogused põllumajanduskäitistest ja lämmastiku potentsiaalne mõju Natura 2000 aladele Eestis), Tallinna Tehnikaülikool, Ehitusteaduskond, Keskkonnatehnika instituut.

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LIST OF PUBLICATIONS

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M. Maasikmets, H-L, Kupri, A. Konist, E. Teinemaa. (2018). Identification of packaging waste and catalytical soot removal powder

tracers in household heaters using ash and filter analyses. International Aerosol Conference. St.Louis, USA

M. Maasikmets, M. Elser, C. Bozzetti, H. Keernik, E.Teinemaa, I. El-Haddad, R. Richter, J.G. Slowik, U. Baltensperger, and A.S.H. Prévôt. (2017). Aerosol chemical composition and spatial distribution in industrial areas using mobile aerosol mass spectrometry. European Aerosol Conference 2017. Zürich, Switzerland

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Maasikmets, Marek; Kaasik, Allan; Ruus, Aime; Teinemaa, Erik. (2013). Seasonal variability of the PMx chemical composition and ammonia concentration in loose-housing cowshed. Digital Handbook EAC 2013, Prague: European Aerosol Conference 2013.

VIIS VIIMAST KAITSMIST

KATRIN KALDRE
INVASIVE NON-INDIGENOUS CRAYFISH SPECIES AS A THREAT TO THE NOBLE CRAYFISH (ASTACUS ASTACUS L.) POPULATIONS IN ESTONIA. INVASIIVSED VÄHI VÕÕRLIIGID JA NENDE OHUSTAV MÕJU JÕEVÄHI (ASTACUS ASTACUS L.) ASURKONDADELE EESTIS
Emeriitprofessor Tiit Paaver, professor Riho Gross
15. juuni 2018

PILLE TOMSON
ROLE OF HISTORICAL SLASH AND BURN CULTIVATION IN THE DEVELOPMENT OF CULTURAL LANDSCAPES AND FOREST VEGETATION IN SOUTH ESTONIA. AJALOOLISE ALEPÕLLUNDUSE ROLL LÕUNA-EESTI MAASTIKE JA METSATAIMESTIKU KUJUNEMISEL
Professor Robert Gerald Henry Bunce, professor Kalev Sepp
24. oktoober 2018

MARI TILK
GROUND VEGETATION DIVERSITY AND GEOBOTANICAL ANALYSIS IN THE SOUTH-WEST ESTONIAN DUNE PINE FORESTS. ALUSTAIMESTIKU MITMEKESISUS JA GEOBOTAATILINE ANALÜÜS EDELA-EESTI LUITEMÄNNIKUTES
Vanemteadur Katri Ots, juhtivteadur Malle Mandre, teadur Tea Tullus
12. detsember 2018

GABRIELLA KOVÁCS
EFFECT OF HOST PLANT AND LAND USE ON CABBAGE SEED WEEVIL INFESTATION AND ASSOCIATED PARASITOIDS. PEREMEESTAIME JA MAA-KASUTUSE MÕJU KÕDRA-PEITKÄRSAKA KAHJUSTUSE JA PARASITEERITUSE TASEMELE
Dotsent Eve Veromann, prof. emeritus Anne Luik
12. detsember 2018

SERGEY KASK
VIRTUAL REALITY IN SUPPORT OF SUSTAINABLE TOURISM: EXPERIENCES FROM EASTERN EUROPE. VIRTUAALNE REAALSUS TOETAMAS SÄÄSTLIKKU TURISMI: IDA-EUROOPA KOGEMUSED
Professor Tiiu Kull, teadur Kati Orru
30. jaanuar 2019

ISSN 2382-7076
ISBN 978-9949-629-64-0 (trükis)
ISBN 978-9949-629-65-7 (pdf)